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Trihalomethane Removal by Coagulation Techniques in a Softening Process

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16. ABSTRACT

Experimental work was conducted on both bench and pilot scale at the Daytona Beach Ralph F. Brennan water treatment plant to determine what combinations of coagulants and water pH could best remove trihalomethane precursor materials.

The following conditions were evaluated with lime softening:

Coagulation with:

- clay plus a cationic polymer
- alum plus a non-ionic polymer
- alum plus low pH
- alum plus high pH
- experimental polymeric coagulant

A two-stage coagulation process, alum added at low pH (ca. 5.0) followed by settling, softening, and settling again, whowed a slight improvement in precursor removal over single-step coagulation and over softening followed by low pH coagulation. Pilot scale performance (i.e. quality of finished water) tended to be poorer than full scale because of no sludge recirculation.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report describes a study conducted in Daytona Beach, Florida which evaluated on a pilot scale improved coagulation techniques in a lime softening process and the effects of these techniques in reducing Trihalomethane formation potential in a ground water supply.

Francis T. Mayo, Director
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PREFACE

In 1979, the U. S. Environmental Protection Agency promulgated an amendment to the National Interim Primary Drinking Water Regulations establishing a maximum contaminant level (MCL) of 0.10 mg/l for total trihalomethanes. Two previous investigations conducted at the Ralph F. Brennan Municipal Water Treatment Plant in Daytona Beach indicated that the level of trihalomethanes in the finished water was several times greater than the MCL.

These reports further concluded that the level of trihalomethane production could be reduced by improving coagulation and by altering the point of chlorination in the treatment process. These treatment modifications would not, however, reduce effluent THM concentrations below the legislated maximum. Rather, they indicated that the precursor compounds, naturally present in the raw water well source used by Daytona Beach were especially resistant to removal through conventional lime softening and coagulation techniques.

This study was subsequently undertaken to:

1. Provide additional supporting data for preliminary conclusions that were based on very limited data;

2. Investigate more fully processes that offered the most promising results for precursor removal in earlier studies; and,

3. Pursue other variations in an effort to meet the established trihalomethane MCL.

The research program was established in three phases: a literature search; jar test experiments; and pilot plant operation. The pilot plant used was the EPA trailer-mounted, twin-process stream coagulation, clarification and filtration facility loaned to the City of Daytona Beach for this test work.

ABSTRACT

This research program was undertaken to determine whether a softening and coagulation process combined with disinfection by chlorination could be developed to produce a treated water that would meet the established trihalomethane MCL of 100 ug/L. The experimental work was conducted at the Daytona Beach Ralph F. Brennan Water Treatment Plant, which draws its raw well water from the Floridan aquifer.

An extensive jar test program was conducted to establish which processes showed sufficient precursor removal efficiency to warrant further dynamic testing in the pilot plant facility.

An experimental polymeric coagulant provided by the Rohm and Haas Company was evaluated as a coagulating system in the lime-softening process both by itself and in combination with a bentonite clay.

A series of eight pilot plant tests was developed as a result of the jar-testing program to evaluate the various treatment alternatives:

1. Simulation of full-scale Brennan Plant conditions for development of baseline data.

2. Clay and a cationic polymer in combination with lime softening.

3. Alum at 20 mg/L with non-ionic polymer, in combination with lime softening.

4. Alum at 40 mg/L with non-ionic polymer, in combination with lime softening.

5. Two-stage coagulation and softening involving low pH coagulation with 40 mg/L alum and sulfuric acid pH adjustment followed by lime softening.

6. Two-stage coagulation and softening involving low pH coagulation with 80 mg/L alum and sulfuric acid pH adjustment followed by lime softening.

7. Two-stage softening and coagulation involving lime softening and coagulation with an anionic polymer followed by 50 mg/L alum and final NaOH pH adjustment.

8. Use of CA-35 clay in conjunction with an experimental coagulant polymeric followed by lime softening.

As expected, the base-line condition showed precursor removal of only about 20 percent.

The other seven pilot plant runs showed varying degrees of improvement over the base-line, however none met the desired goal of 100 ug/L effluent THM concentration. The eighth run came closest, with an average effluent THM of 158 ug/L. The use of this process is nonetheless likely to enable the Brennan plant to comply with the established MCL, since efficiency is gained through fullscale operation, and since actual distribution system THM values are lower than realized in the test work.

This report was submitted in fulfillment of Contract No. CR 80742601 by the City of Daytona Beach under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period from October 10, 1980, through July 19, 1982, and work was completed July 19, 1982.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ACSC	-- alum clarifier super chlorinated, stored 72 hours
Alum	-- aluminum sulfate
Ferric	-- ferric sulfate
FWID	-- finished water immediately dechlorinated
FWSC	-- finished water super chlorinated, stored 72 hours
GC	-- fas chromatograph
gpm	-- gallons per minute
LSSC	-- lime clarifier super chlorinated, stored 72 hours
MCL	-- maximum contaminant level
MGD	-- million gallons per day
MGL	-- million liters per day
mg/L	-- milligram per liter
NTU	-- nephelometric units
PCU	-- platinum cobalt units
RWSC	-- raw water super chlorinated, stored 72 hours
THM	-- trihalomethane - For purposes of this Study, this is restricted to the following: Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Dibromochloromethane ($CHBr_2Cl$), Bromoform ($CHBr_3$)
THMFP	-- trihalomethane formation potential
TOC	-- total organic carbon
ug/L	-- microgram per liter
UV	-- ultraviolet

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SECTION 1

INTRODUCTION

In November 1974, the U. S. Environmental Protection Agency initiated the National Organics Reconnaissance Survey (NORS), which identified the presence of certain halogenated organic compounds in drinking water samples collected from 80 cities in the United States. The most prevalent of these compounds was a group identified as trihalomethanes (THMs). Since that time, a considerable amount of research has been devoted to identifying methods for removing these compounds once they have been formed in water treatment processes, preventing their formation by removing the organic material (precursor material) already present in the water source, and investigating the use of disinfectants other than chlorine.

Of these three broad treatment options, removal of the precursor material is generally the most attractive both from an operational standpoint and from a water quality standpoint. Most of the larger water treatment plants in the United States have provisions for coagulation already in their treatment processes and would require a minimal capital expenditure to reduce THM formation to meet the 100 ug/L maximum contaminant level (MCL) established by EPA, provided that coagulation can be shown to be effective in removal of THM precusors.

Two studies funded by EPA have been performed in the past at the Daytona Beach Ralph F. Brennan Plant, a 45.4 ML/D (12 MGD) municipally-owned water treatment plant. Work was directed to minimize THM formation in a typical Florida precipitative lime softening plant drawing from a moderately colored ground-water source. The conclusions of these studies were that by changing the point of chlorination in the plant and improving coagulation, THM formation could be reduced somewhat. But no treatment scheme was identified that would reduce this formation enough to bring the water system into compliance with the MCL.

The purpose of this study was to further pursue work done on removing precursor material from a colored ground-water source. The approach was to optimize coagulation in conjunction with lime softening to identify a treatment scheme that would allow this water system and those like it to comply with the 100 ug/L THM regulation now in effect.

SECTION 2

CONCLUSIONS

1. Based on results of this study obtained from the use of EPA's mobile water treatment plant:

    a. The water source that was studied in the project is extremely difficult to work with from the standpoint of removing precursor material by coagulation processes. Because it was beyond the scope of this project to identify individual precursor compounds, it could not be determined whether there was a preferential removal of specific precursors by any specific process. Nevertheless, a simple change in coagulants used in the treatment scheme will not be sufficient to significantly reduce precursor material in this water system.

    b. A two-step coagulation process making use of alum added at low pH followed by settling, softening, and settling again showed an improvement in precursor removal efficiency over single-step coagulation and over softening followed by coagulation. But the slight improvement realized must be weighed against the loss in plant capacity this would cause and the high capital cost involved in plant modifications.

    c. Use of the experimental polymeric coagulant evaluated in this study will probably bring this water system into compliance with the 100 ug/L THM MCL.

    d. Pilot plant precursor removals tend to be lower than plant-scale removals. This is most likely due to the lack of sludge recirculation in the pilot plant.

2. Although a correlation exists between UV absorbance and THMs, and between TOCs and THMs, neither of these surrogate parameters can be used with confidence to predict THM's for this system.

3. The scope of this project did not include identifying individual precursor compounds in this water supply and determining their origin. But it was noted that an inverse correlation exists between local rainfall and THM formation potential (THMFP). During rainy months when more water recharged the well field, it was quite apparent that this

water had less THM precursor material. The opposite occurred during dry weather when the water remaining in the cypress swamps picked up more organic material from decaying vegetation, with an accompanying increase in THMFP.

SECTION 3

RECOMMENDATIONS

1. Work should be directed to identify the precursor compounds present in the raw water to determine whether individual processes preferentially remove specific THM precursors.

2. Further effort should be devoted to studying the performance of Rohm & Haas Polymeric Coagulants for precursor removal. Avenues that still need to be explored include:

    a. The possible synergistic effect realized by the use of clay with these coagulants.

    b. The possible reduction of coagulant dose through the use of other inorganic coagulants in conjunction with this polymer.

    c. Effects of dilution, point of addition, mixing speeds, and sludge recirculation.

    d. The problem noted of turbidity breakthrough of filters.

    e. The possible benefits to be realized if the chlorine demand of this water can be reduced.

    f. The possible reduction in precursor compounds through use of an intermediate filtration step.

    g. Full-scale plant trial of the resins with extensive monitoring in the plant and distribution system.

SECTION 4

BACKGROUND

GENERAL APPROACH

The basic approach used in this study involved a three-step process:

1. Identification of potentially successful methods for the removal or reduction of the organic precursors for trihalomethanes by coagulation, based on review of technical literature and water treatment experience of the project staff;

2. Bench-scale evaluation of candidate treatment methods identified in Step 1; and,

3. Pilot plant evaluation of the treatment methods which yielded positive results in bench-scale tests.

REVIEW OF LITERATURE AND IDENTIFICATION OF CANDIDATE TREATMENT METHODS

Numerous studies have been published in the technical literature over the last several years which document the effectiveness of coagulation for precursor removal. Kavanaugh[1] (1978) reviewed the literature and discussed several plant-scale studies in California showing that coagulation with hydrolyzable metal salts (aluminum and ferric) reduced the concentration of THM precursors. The optimum conditions were, as anticipated from many earlier color removal studies, stoichiometric with respect to dosage and at low pH values (pH 4 to 6). Removal of organics by coagulation ranged from 40 to 90 percent, with efficiency of removal strongly influenced by the pH, the specific coagulant and its dose, and the coagulant-polymer combination.

Studies by Babcock and Singer[2] (1979) showed that alum coagulation would consistently remove greater than 70 percent of the THM precursors present in prepared solutions of humic and fulvic acids which are the predominant organic compounds in most waters. Simultaneous removal of total organic carbon (TOC) varied greatly, from 22 to 86 percent. TOC removal very closely paralleled color removal by coagulation with alum, while a substantial amount of TOC presisted for the fulvic acid fraction. It appears that only a portion of the fulvic acid fraction can be precipitated by coagulation. Thus, humic fractions respond better to coagulation than the fulvic fractions. The percent removal of organic compounds by alum coagulation varied also according to the relative size of the compound. Generally,

larger organic compounds (i.e., humic acids) were more readily coagulated than samller ones (i.e., fulvic acids). In addition, a pH of 5.5 or lower was found to be necessary for optimum coagulation of humic acids, while a pH of 5.0 or lower was needed for effective coagulation of fulvic acids. A pH above this range resulted in ionization of the humic and fulvic acids, giving them a negative surface charge and making them less susceptible to coagulation and flocculation.

Semmens and Field[3] reported success in reducing precursors in Mississippi River water using alum doses higher than those generally used for turbidity removal. Success was highly dependent on pH and dose.

In addition to these studies, many other studies have been performed on coagulation of THMs (see Bibliography for additional references on THMs). Generally, the studies have shown that coagulation of THM precursors is a function of coagulant dose and pH. The stuides have also demonstrated the high variability of response of different waters to coagulaion. The precursors in some waters may be easily removed while precursors in other waters may be relatively unaffected by coagulation.

Earlier studies by Brodeur[4] (1978) showed that the use of alum as an additional coagulant in the Daytona Beach Water Treatment Plant reduced the concentration of THM's in the plant effluent and in samples stored for 24 hours. Although there were problems with the THM analytical results, it was apparent that some benefit was achieved. The system was not optimized though which led to the need for the study reported here.

DESCRIPTION OF WATER SOURCE

The City of Daytona Beach owns and operates two water treatment plants, the newest of which is the Ralph F. Brennan Plant (dedicated in 1976). A common water source supplies both plants through a single raw water transmission main. A total of 12 "deep" wells extending into the Avon Park limestone formation (a portion of the Floridan aquifer) an average of 64 m. feed this raw water main. Each well is 40.6 cm in diameter and cased to a depth of about 33.5 m. The remaining depth is an open hole in the solid limerock formation.

These 12 wells are located in a line running roughly east and west from 5.6 Km to 14.5 Km from the Atlantic Coastline. Although they feed into a common line, the four westernmost wells actually supply the Brennan Plant. These four wells are located on a ridge called Rima Ridge which separates two terraces. One of these, the Talbot Terrace, is a broad expanse of swampy land with an ill-defined drainage pattern. This is an area with a high recharge rate to the Floridan aquifer and the dark, teacolored swamp water is apparently responsible for much of the color found in Daytona's raw water. In passing through this swampy area the water's pH is depressed, presumably by the naturally occurring weak organic acids such as humic and tannic acid, but then is neutralized as it migrates downward to the Floridan

aquifer through underlying limestone formations. This neutralization process is responsible for the relatively high hardness and alkalinity found in the raw water; see Table 1 - Water Analysis. Raw water quality with respect to alkalinity and total hardness generally remains within a 10 percent variation.

STATISTICAL METHODS

Various methods of compiling analytical data and rejection of outliers were considered. In each of the pilot runs as well as in the jar test work, the number of samples collected and analyzed was limited by time and laboratory costs. Thus, for any given condition, no more than a dozen sets of samples were obtained. Wide variations frequently observed in such a small sample size precluded rejection of outliers on a deviation from the mean basis.

Lack of historical analytical data prevented the determination of a meaningful estimated variance, so this method of data rejection was similiarly discarded. Dixon's and Chouvenet's criteria were also considered inappropriate because of the normal distribution assumptions necessary.

Consequently, all values reported are the arithmetic mean of raw data, without statistical rejection of any outliers. Only THM values on samples showing no free chlorine residual and other data known to involve laboratory errors were eliminated.

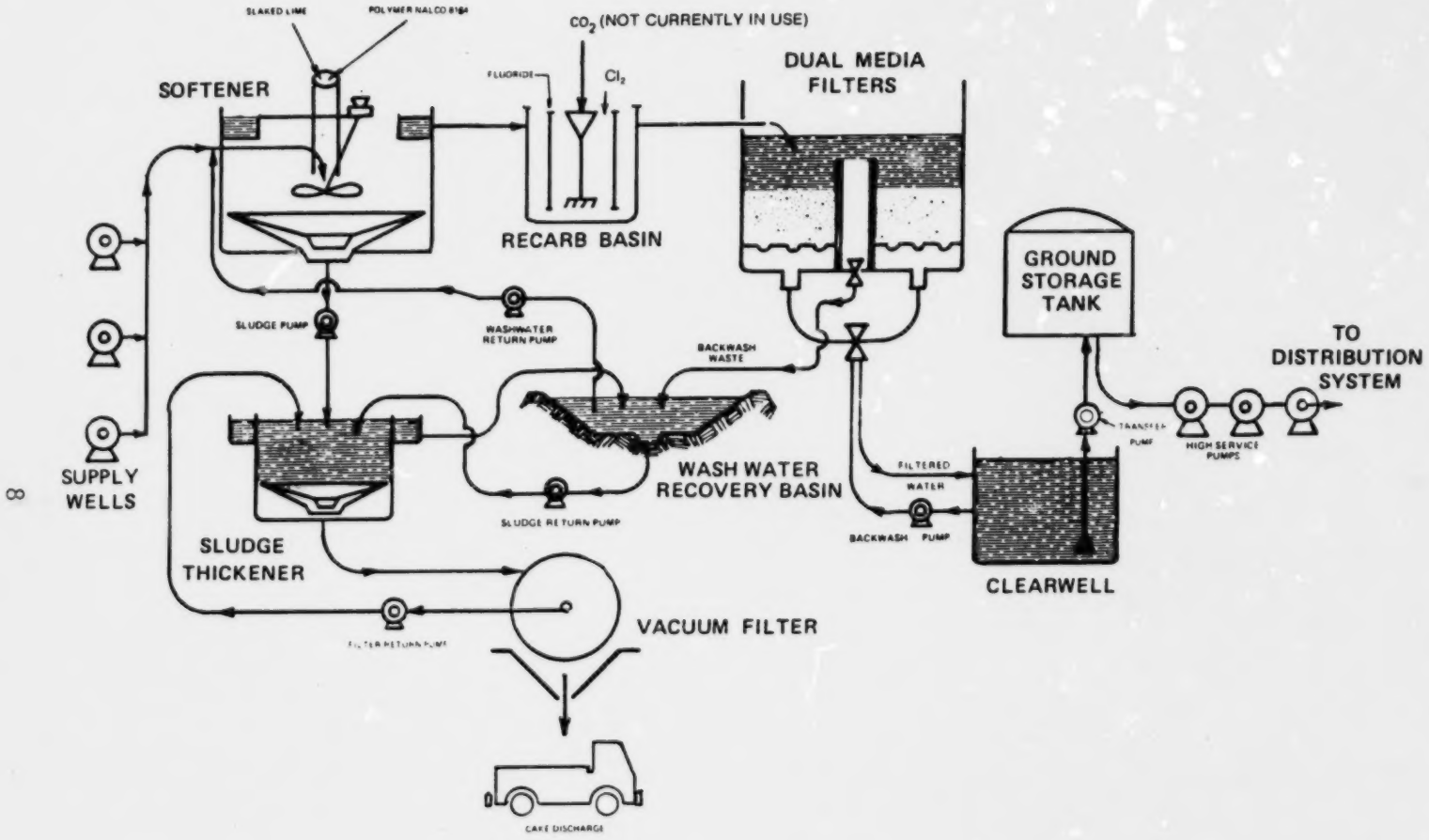


FIGURE 1 Flow diagram of Ralph F. Brennan Water Plant, Daytona Beach, Florida.

TABLE 1. RAW WATER ANALYSIS - YEARLY COMPARISON

Parameter	5/76	11/77	8/78	5/79	10/80	11/81
pH	7.3	6.8	7.0	7.1	6.9	6.8
Color, PCU	34	20	20	15	15	15
TDS, mg/L	392	323	424	362	383	452
Turbidity, NTU	1.8	0.26	0.25	0.4	0.3	0.1
Total Hardness, mg/L as $CaCO_3$	294	316	284	298	294	296
Calcium, mg/L as Ca^{+2}	104	114	101	95	111	102
Magnesium, mg/L as Mg^{+2}	8.5	7.2	7.4	14.3	3.8	9.5
Alkalinity, mg/L as $CaCO_3$	276	254	274	260	276	274
Chloride, mg/L	50	37	33	42	36	54
Sulfate, mg/L as So_4^{-2}	2.0	4.3	4.3	2.0	9.8	6.2

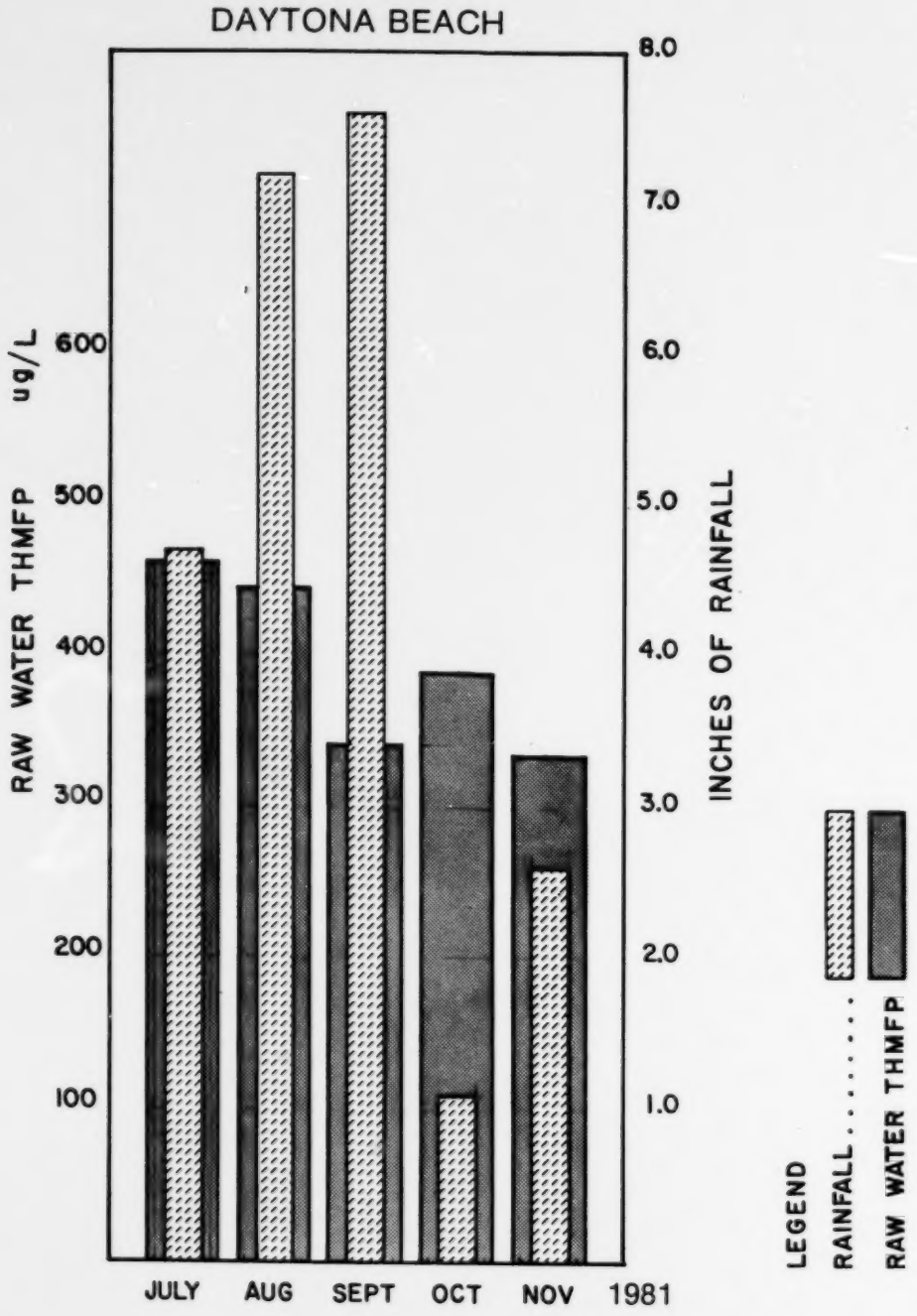


FIGURE 2 Inverse correlation between rainfall and THMFP.

SECTION 5

JAR TEST PROGRAM

Based on the review of the literature and the project team's experience, it was decided to test, on a bench-scale level, several operational parameters and conditions for their effect on precursor removal including:

1. Aluminum sulfate (alum) vs. ferric sulfate (ferric) as a coagulant;

2. Coagulant dose (alum and ferric);

3. Coagulation pH (alum and ferric);

4. Coagulation followed by lime softening;

5. Lime softening followed by coagulation;

6. Softening at a high pH (approximately 11) with magnesium carbonate;

7. Several other coagulant aids including sodium aluminate, polymers;

8. Bentonite clay followed by a Cationic polymer.

A two-stage jar test program was performed at the Brennan Water Treatment Plant, Daytona Beach, Florida, to evaluate potential water treatment processes for THM precursor removal and to aid in selecting the treatment processes to be tested in the pilot plant study. The jar tests were conducted in two-liter, square, Plexiglas jars equipped with magnetic stirrers on a Turbitrol jar test machine (see Appendix for detailed procedures). Subsequent jar testing was performed using a six-place Phipps and Bird gang stirrer with 21 square glass jars. Chlorinated samples collected in the first and second stage for testing were stored 48 hours to approximate residence time in the distribution system. Later work indicated this time to be closer to 72 hours, therefore, subsequent jar test samples and all samples collected during the pilot plant study were stored for 72 hours prior to dechlorination.

FIRST STAGE TESTING

The first stage of the jar test program was initiated in late December 1980. A series of six sets of jar tests was conducted. Each set consisted of six jars, with the exception of the sixth set, which consisted of three jars.

The initial set was designed to determine the optimum dose of lime required for softening raw water. The lowest total hardness (48 mg/L) was obtained using a lime dose of 250 mg/L. The total THM concentration for this sample was 629 ug/L, indicating that a significant amount of THM precursors was not removed by lime softening. Residual color in this set of jars ranged from 20 to 28 PCU.

The second set of jars was designed to determine the influence of pH on color and THM precursor removal from raw water coagulated with a fixed dose of coagulant. Three jars were coagulated using 30 mg/L of alum at pHs of 6.1, 5.8, and 5.4. Three additional jars were coagulated with 30 mg/L of ferric at pHs of 6.1, 5.8, and 5.5. In the jars using alum, lower pH resulted in both lower residual color and lower THM formation, but the concentrations of THMs show that there is a substantial quantity of precursors not removed during the coagulation process. In the jars using ferric as with alum, fewer THMs were formed at lower pH, however, color removal was generally inadequate. Coagulation of color using ferric is usually more effective at a pH lower than that achieved in this test. The data show that, as with alum, THM concentration was still too high. Additional testing with ferric at a lower pH was conducted later in the jar test program.

The third set of jars was designed to determine the influence of alum dose and pH on color and THM precursor removal when coagulating settled (softened) water with alum.

Three jars of settled, softened water were coagulated with 30 mg/L of alum and 0.3 mg/L 985 N (manufactured by American Cyanamid Company) at pHs of 6.1, 5.8, and 5.6. Color was reduced from 21 to 5 PCU for all three jars, indicating that the pH of coagulation for settled water is not as important a control variable as the pH of coagulating for raw water. The analytical data for THMs show that coagulation with alum did not remove an adequate quantity of THM precursors from the settled water in order that the THMs resulting from subsequent chlorination would meet the MCL.

Three jars were coagulated with 20, 40, and 50 mg/L alum and 0.3 mg/L 985 N. Color removal varied directly with alum dose. THM concentrations again show that an adequate amount of precursor material was not removed by coagulation.

In the fourth set of jar tests, it was decided to test the effect of coagulation (with alum) followed by softening on the removal of THM precursors. Six jars of raw water were coagulated with alum doses of 5, 10, 15, 20, 25, and 30 mg/L and 0.3 mg/L 985 N. After coagulation, flocculation, settling, and decanting the six water samples were each softened at a pH of 9.0 - 9.2 by the addition of 220 mg/L of lime, 0.3 mg/L Nalco 844A, and

approximately 4 grams of $CaCO_3$ sludge. THM concentrations averaged approximately 300 ug/L. One sample had a concentration of 74.8 ug/L; however, this datum is inconsistent with the other five samples tested in this set and is suspect.

The effect of using clay and CatFloc-T was tested in the fifth set for use as aids in the softening process. The effect of adsorption of color by clay has been reported in the literature[5], indicating a potential for precursor removal. In three jars, the dose of clay (Ca 35) manufactured by Calgon Corporation, was kept at 1 mg/L, while CatFloc-T was added at concentrations of 0.5, 1.0, and 1.5 mg/L. In three other jars, the dose of CatFloc-T was kept constant at 1.0 mg/L, while clay was added in concentration of 0.5, 1.0, and 1.5 mg/L. In all jars, the clay was added prior to rapid mixing, the CatFloc-T was added during rapid mixing followed by approximately 4 grams of $CaCO_3$ sludge and then 250 mg/L of lime. THM concentrations were somewhat lower than that achieved by using lime only.

Finally, a sixth set of three jars were run using settled plant water. One jar used sodium aluminate as a coagulant. Color was reduced to 25 PCU. The THM concentration from this test was 614 ug/L, indicating that sodium aluminate is no more effective as a coagulant than alum or ferric with respect to precursor removal. No further testing was performed with sodium aluminate.

SECOND STAGE TESTING

After evaluating the results of the first stage of testing, a second program of jar tests was developed and was conducted during early February, 1981.

Additional tests were conducted with ferric to determine whether it could effectively remove THM precursors under more favorable conditions (lower pH) than those achieved in the December 1980 jar tests. Six jars of raw water were coagulated with 30 mg/L of ferric at pHs ranging from 4.0 to 6.2. THM concentrations from all jars were over 600 ug/L. The lowest residual color obtained using ferric was between 25 and 30 PCU. Three additional jars of raw water were coagulated using ferric doses of 20, 30, and 40 mg/L with the pH between 5.1 and 5.2 to determine the effect of ferric dose at a relatively fixed pH. THM levels in the samples were all greater than 500 ug/L. It was concluded that even under optimal conditions, ferric was no more effective as a coagulant for precursor removal than alum and was less effective than alum for color removal.

The effect of adding magnesium ($MgSO_4$) and sodium carbonate (Na_2CO_3) to raw water and raising the pH of softening to approximately 11.2 was evaluated in two jars. Five and 10 mg/L of magnesium (as Mg^{2+}) were added to two jars, with 400 mg/l lime, approximately 5 g of $CaCO_3$ sludge, and 60 mg/L of Na_2CO_3. THM concentrations for samples from these jars were 224 ug/L and 215 ug/L, respectively. These THM concentrations are substantially

(approximately 400 ug/L) better than those obtained by softening with lime only. Additional studies were conducted with Mg^{2+}, without adding Na_2CO_3. The THM concentrations for those tests, with one exception, ranged from 458 ug/L to 666 ug/L. These results suggested that, if additional precursor removal can be obtained by pre- or post-coagulation, softening with magnesium, lime, and soda ash may be an effective process for THM control.

Because the initial two jar test results using magnesium sulfate and sodium carbonate were so promising, further jar test work was conducted. However, it should be noted that these samples had a 48-hour storage time rather than the 72 hours used in subsequent testing. Results of these subsequent tests did not substantiate the earlier finding and efforts in this direction were abandoned.

THIRD STAGE TESTING

Jar Testing - (Conditions 5, 6 and 7)

In August 1981, a meeting was held involving consultants, city personnel, and the project officer. Past conditions of the pilot plant were discussed as well as subsequent treatment schemes. Among items discussed was the importance of optimizing the alum dose as well as the pH during the coagulation process. This discussion during the meeting initiated additional jar testing to define optimum coagulation conditions.

The first set of jars was designed to determine the influence of various alum doses at two different pHs for precursor removal. Doses ranging from 20 mg/L to 100 mg/L at increments of 10 mg/L were evaluated at pHs of 5.0 and 5.5. THM results ranged from 192 ug/L to 327 ug/L. Optimum dose was 80 mg/L at a pH 5.5. At a pH 5.0 80 mg/L of alum resulted in the lowest THM concentration of 197 ug/L. Anticipating pH adjustment problems, the 80 mg/L alum dose was selected, maintaining a pH range of 5.0-5.5 during coagulation to represent Condition 6.

Subsequent jar tests were performed in an attempt to settle the fine alum floc formed when alum was used as a coagulant on the raw water. Three polymers, Percol LT 22S-cationic, Percol LT 24-cationic, and Percol LT 27-anionic, were added at doses of .05 mg/L and .10 mg/L to jars containing an 80 mg/L alum dose and pH adjusted to 5.5. Fine particles still remained suspended with no apparent settling. A 5 mg/L dose of clay (Ca-35) was then added in an attempt to settle the fine floc; however, results were still poor.

During Conditions 5 and 6, there was a significant increase in final effluent hardness results. A set of jars was set up to define the point of formation of this additional hardness. The hardness data collected was as follows: Raw water - 288 mg/L, alum-coagulation process effluent - 260 mg/L to 288 mg/L, lime-softening process effluent - 272 mg/L to 500 mg/L, and final effluent - 282 mg/L to 504 mg/L. Total alkalinities remained low indicating that carbonate hardness was being removed during the lime-soften-

ing stage. To account for the increase in hardness, however, non-carbonate hardness must have developed in the lime-softening process.

Two sets of jars were evaluated to define Condition 7, softening at a high pH followed by coagulation at a low pH.

Five jars of raw water were softened using lime to raise the pH to 9.4. Nalcolyte 8184 was added at .08 mg/L as a coagulant aid. After settling, the suppernatant was decanted and pH adjusted to 5.0 before adding alum at various doses. Alum doses ranged from 40 to 80 mg/L in 10 mg/L increments. THM results revealed to 50 mg/L alum dose to optimum. THM values ranged from 116 ug/L to 279 ug/L.

The Brennan Plant clarifier effluent was used in the second set of jars to represent softening at a high pH (9.3). The softened water was adjusted to pH values from 6.0 to 9.5 in increments of .5 pH units before an 80 mg/L alum dose. THM results ranged from 48.2 ug/L to 193 ug/L. Optimum coagulation pH proved to be 5.5, however, pH values of 8.0 and 7.5 resulted in THMs of 71.9 ug/L and 70.4 ug/L, respectively.

After evaluating the jar testing data, Condition #7 was defined as follows: lime softening with a 220 mg/L lime dose at pH 9.3 followed by alum coagulation with a 50 mg/L alum dose at a pH range of 7.5-8.0. Selecting a coagulation pH range of 7.5-8.0 over the optimum 5.5 pH made possible the elimination of an acid feed system.

Condition 8 - Jar Tests

Condition #8 involved the use of experimental Polymeric coagulants developed by the Rohm and Haas Company which required an extensive jar testing program to define optimum conditions. These coagulants (XE 391 and XE 392) are insoluble cross-linked polyelectrolytes containing acidic or basic funtional groups. The basic form (XE-392) of these coagulants interacts with negatively charged humic compounds to form a floc which, with the aid of small doses of the acidic form (XE-391) becomes dense enough to settle and be removed as sludge. Seven sets of jars were evaluated prior to setting up Condition 8 in the pilot plant.

The first set of jars duplicated the suggested doses by the manufacturer using Daytona Beach raw water. XE-392 was added to the raw water at doses of 10, 15, 20, 25 and 30 mg/L. Sufficient XE-391 was added to tie up unreacted base functional polymer and aid the settling of the floc. Slaked lime was then added at a dose of 220 mg/L for softening purposes. THM results were significantly higher than data presented by the manufacturer, and the floc formed did not settle readily as reported. THMs in our jar testing ranged from 130 ug/L to 242 ug/L; a 30 mg/L XE-392 dose produced the lowest THMs.

A second set of jars was conducted expanding the XE-392 dose to 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/L. The XE-391 was eliminated. THMs ranged

from 139 ug/L to 308 ug/L, indicating an optimum dose at 20 mg/L producing 139 ug/L THMs.

The higher than expected THM results and the difficulty experienced in settling the floc resulted in the third set of jars run as a joint effort between Rohm and Haas personnel and the City. One jar received 5 mg/L clay (Ca-35) dose prior to polymer and lime addition. The second jar received an overdose of clay prior to plymer and lime addition. THMs for the first jar were 26.5 ug/L, the second jar were 45.7 ug/L.

The fourth set pursued the idea of the raw water being dosed with clay prior to polymer and lime addition. A 5 mg/L clay dose was chosen since prior approval from the Florida Department of Environmental Regulation had been obtained for use of this clay in potable water at dosages up to 5 mg/L. Nine jars were dosed with 5 mg/L clay, each followed by the addition of various XE-392 doses, ranging from 10 mg/L to 50 mg/L in increments of 10 mg/L. A dose of 4.5 mg/l XE-391 followed the addition of the XE-392 resin. All jars were then lime softened with 220 mg/l lime at a pH of 9.4, samples were decanted, chlorinated and stored 72 hours. THM results ranged from 37.4 ug/L to 145 ug/L. A 30 mg/L dose of XE-392 produced the lowest THM values, 37.4 ug/L; however, a 20 mg/L dose produced only 50.4 ug/L.

The fifth set included two jars. A jar was run duplicating optimum conditions found in the fourth set, with the exception of the point of addition of the XE-391. This coagulant was added after the softening process as opposed to just before as in the fourth set. The results indicated that adding the XE-391 prior to softening produced lower THMs. The second jar looked at alum in addition to clay, polymer and lime in precursor removal. Raw water was dosed with 80 mg/l alum followed by 5 mg/l clay, 30 mg/l XE-391, 4.5 mg/L XE-392, and 220 mg/L lime. THMs produced were 44.4 ug/L suggesting that alum does not provide additional precursor removal when used in conjunction with the coagulants. Work currently being pursued in this area, however, indicates that other inorganic coagulants added in addition to the XE-392 can be used to lower the XE-392 dosage.

The sixth set examined various clay doses with a 30 mg/L XE-392 dose and a 4.5 mg/L XE-391 dose. Clay doses of 2, 4, 6, 8 and 10 mg/L were tested in relation to final effluent turbidities. Turbidities ranged from 32-50 NTUs, indicating a possible increase of solids loading on the filters as opposed to the previous conditions.

The seventh set of jars was to evaluate optimum XE-391 doses in conjunction with 20 mg/L and 15 mg/L XE-392 dose. Order of chemical addition was as follows: 5 mg/L clay, 20 or 15 mg/L of XE-392 resin, five different doses of XE-391 for each XE-392 dose, and 220 mg/L lime. The 20 mg/L XE-392 dose produced THMs from 97.8 ug/L to 242 ug/L with optimum XE-391 dose being 3.5 mg/L. The 15 mg/L XE-392 produced THMs from 63.3 ug/L to 174 ug/L with optimum XE-391 dose being 0.5 mg/L.

Reviewing the data from the jar tests, Condition #8 represented the following treatment scheme: 5 mg/L clay, 20 mg/L XE-392, 3.5 mg/L XE-391 and 220 mg/L lime.

Following the pilot plant study of Condition #8, two additional sets of jar tests were run. The first set tested the effect of various clay doses in conjunction with the base functional polymer and lime on precursor removal. six jars involved clay doses of 10, 15, 20, 25, 30 and 35 mg/L with 20 mg/L XE-392 and 220 mg/l lime. six other jars used the same clay doses with 15 mg/L XE-392 and 220 mg/l lime. The 20 mg/l polymer series produced THMs from 218 ug/L to 266 ug/L, optimum being a 35 mg/L clay dose. The 15 mg/L polymer jars resulted in THMs from 241 ug/L to 311 ug/L, optimum being a 20 mg/L clay dose. The significantly higher THMs produced in this jar set indicated the need for the two polymer combination for most effective precursor removal.

The second set of jars evaluated the effect of chlorinating prior to filtration versus after filtration in relation to THM production. This was of particular interest since the Brennan plant normally chlorinates ahead of filtration to control algae growth in the mixed media filters. For this jar test series filtration was accomplished using Whatman #1 filter paper. Raw water was treated with 5 mg/L clay followed by 20 mg/L XE-392, 3.5 mg/L XE-391 and 220 mg/L lime. Samples chlorinated before filtration produced an average of 240 ug/L THM's. Samples chlorinated after filtration resulted in an average of 188 ug/L THM's.

Filtration seemed to improve the precursor removal by as much as 20 percent, indicating that adequate turbidity capture is very important in making the most efficient use of these coagulants.

ADDITIONAL JAR TESTING

The jar testing program for Condition #8 initiated an interest in reevaluating Condition #2 where a 1 mg/L clay dose was added prior to softening. Six jars were set up and clay added at the following doses: 2, 4, 6, 8, 10 and 12 mg/L. For this seris of jars a filtration step was included using Whatman #1 filter paper. A 220 mg/L lime dose was applied for softening purposes. After filtration, samples were collected and analyzed for turbidity and 3- day stored THM formation. Turbidities ranged from 2.3 to 5.4 NTUs. A 1,000 ml aliquot of settled water from the first six jars was then dosed with 1 mg/L of CatFloc-T in an attempt to reduce the final turbidities. After filtration, samples were again tested for turbidity and 3-day stored THM formation. These turbidities ranged from 1.1 to 2.2 showing a significant improvement using the CatFloc-T.

The THM results from the first set of samples were inconclusive due to a lack of free chlorine residual after three days. However, the second set of samples did exhibit a free chlorine residual after 3-days with THM's ranging from 227 to 366 ug/L. Both sample sets received a 15 mg/L chlorine

FIGURE 3 Precision weighing of jar test chemicals.

FIGURE 4 Adding chemicals to jars.

dose prior to storage. Interestingly, the clay seemed to create a chlorine demand unless tied up by the cationic polymer. The THM results were comparable to Condition #2; therefore, a pilot plant trial was not pursued.

Another set consisting of four jars evaluated the effect of $MgCO_3$ at a pH of 11.2 on precursor removal. Doses of 5, 10, 15 and 20 mg/L were added to five jars with a lime dose of 400 mg/L. THM concentrations ranged from 274 ug/L to 563 ug/L. The results did not prove any more promising than the previous conditions investigated, therefore, a pilot plant trial was not initiated.

In February 1982, a meeting was held at Municipal Environmental Research Laboratories of Cincinnati to review the progress of the project. The difficulty experienced in settling the fine alum floc received much discussion. Suggestions included additional jar testing to determine if the alum floc contained the THM precursors. This could be evaluated by adding a filtration step after coagulation and prior to any pH increase for stabilization or softening purposes which could be dissolving the alum floc, thereby negating any scavenging effect of the presursors by the alum. Two sets of jar tests were run to investigate possible benefits to be realized by an intermediate filtration step.

The first set of jars included the following: #1 - untreated raw water, #2 - Raw water lowered to pH 5.5 during mixing and settling, #3, 4, and 5 received alum doses of 20, 40, 80 mg/L alum respectively with a pH 5.5 for coagulation. From these five jars filtered (.45 micron Millipore membrane) and non-filtered samples were collected, pH adjusted to 8.5, dosed with 30 MG/L chlorine and stored for 3 days. Final THM's showed only a 5% difference between the filtered and non-filtered samples with the minimum THM's being 264 mg/L. Filtration after coagulation did not substantially reduce THM formation, however a significant difference in chlorine demand was exhibited. Free chlorine residuals in the filtered samples ranged from 3.0 mg/L in the raw water to 13.2 mg/L in treated samples after 3 days storage. In the non-filtered samples dosed with the same amount of chlorine, free residuals ranged from 0.2 mg/L to 0.6 mg/L.

A second set of jars was set-up to determine the effect on THM formation by a simple 10 mg/L reduction in chlorine dosage. Two jars were run: #1 - raw water untreated and #2 raw water dosed with 80 mg/L alum, pH of coagulation 5.5. Samples were filtered through the millipore 0.45 micron membrane, pH adjusted to 8.5, dosed with chlorine and stored for three days prior to analysis. Two sets of samples were stored from each jar, one set receiving a 20 mg/L chlorine dose and the other a 30 mg/L chlorine dose.

The results were as follows: #1 - Raw untreated, 20 mg/L Cl_2 Dose, 462 ug/L THMS; #2 coagulated raw water, 20 mg/L chlorine dose, 235 ug/L; #3 -Raw untreated, 30 mg/L Cl_2 dose, 507 ug/L THMS' #4 - Coagulated raw water, 30 mg/L Cl_2 dose, 275 ug/L THMS. A 9% difference in THM production occurred in the untreated raw water samples; a 14.5% difference in the alum dosed samples. A reduced initial chlorine dose resulted in lower THM production.

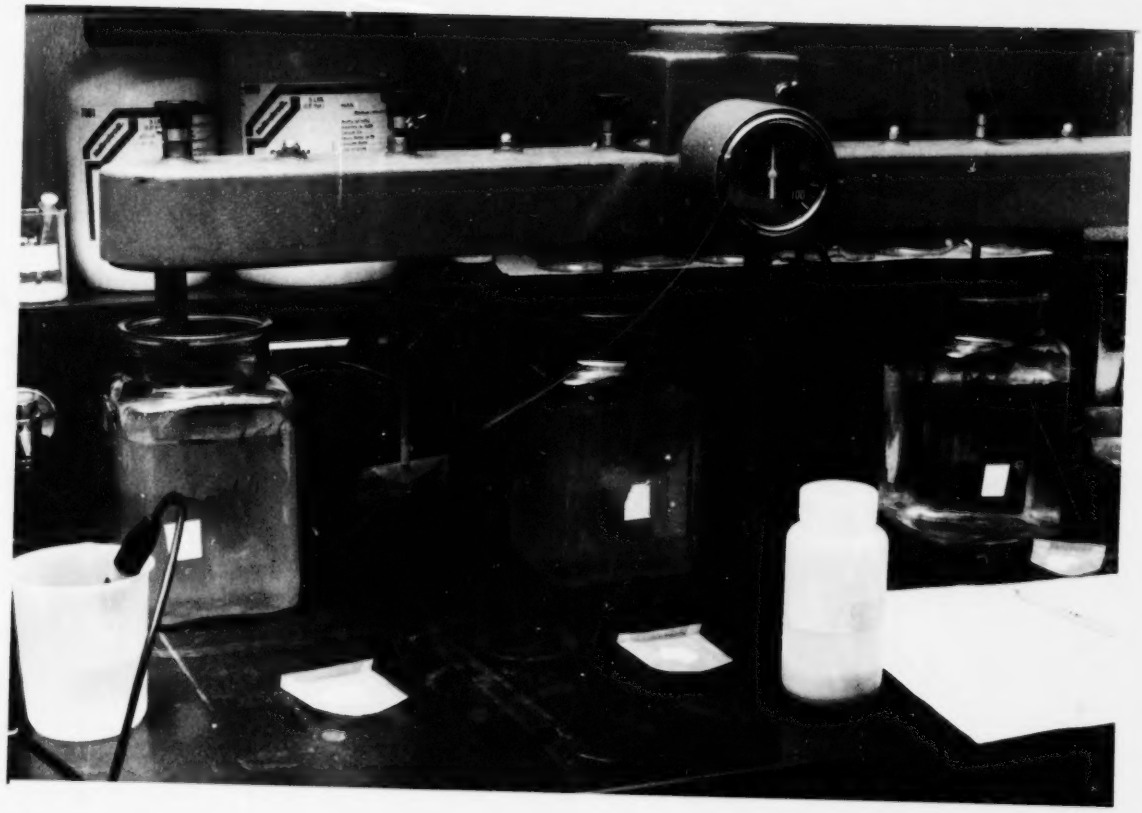


FIGURE 5 Jar testing in progress.

SECTION 6

PILOT PLANT DESCRIPTION

The pilot plant used in this study was a 0.63 Lps water treatment facility fabricated for EPA to be used in water treatment research projects such as this and is housed in a 12.8 m long, eight-wheel trailer. The plant is composed of two identical water treatment system which can be operated independently of each other or in series. All of the treatment units, pumps, valves, and interconnecting piping are of stainless steel construction. (For a more detailed description of this plant, refer to the Appendix.) This pilot plant is extremely flexible in its treatment capabilities, allowing easy set up for each of the conditions studied in this project.

The pilot plant was set up on the Brennan Water Plant grounds and a 5 cm line from the plant's raw water supply was used to provide raw water throughout the study.

Raw water pressure in the supply line was usually sufficient to maintain a 0.32 Lps feed rate in the pilot plant; however, it was decided to use the raw water pump supplied with the trailer to boost and maintain a more constant pressure.

The chlorine used throughout this project was supplied from a 150 lb. cylinder of liquid chlorine housed outside the trailer. An adjustable chlorinator mounted on the cylinder was set to give the maximum feed rate. Plant-furnished water was used to operate an educator which operated the chlorinator. The educator discharged to a 19 liter carboy equipped with a level control switch connected to a solenoid valve which regulated the water supply. This arrangement produced a high-strength chlorine solution which was metered through a chemical feed pump to control the chlorine dose fed in the pilot plant.

Chemical feed pumps used throughout the study were of two types. Diaphragm pumps were used for chemical solutions. Lime and clay slurries (which proved to be impossible to feed continuously through the diaphragm pumps) were fed by peristaltic pumps which gave quite satisfactory results.

One inherent weakness in the pilot plant noted quite early in the project is in the interconnecting piping between tanks. The connections between the rapid mix and flocculation tanks and between the floc tanks and clarifier in each plant are so small in diameter that the lines clogged very quickly with sludge if any chemical treatment was administered in the rapid mix tanks, particularly where lime softening generated $CaCO_3$ sludge. Here

the problem became so severe that it was nearly impossible to continuously operate the plant for periods much longer than two weeks at a time. After two weeks, the plant had to be drained and thoroughly cleaned. It was also found that sludge could not be removed from the clarifiers without first draining the tanks. This hindered any attempts at sludge recirculation during plant operation. In fact, the lime sludge produced from this water was so dense that it could not be coaxed out of the clarifier by way of the drain line provided even with the aid of a fire hose and high pressure water. Accordingly, sludge could only be sampled at the end of each pilot plant run to determine the formation potential of the sludge.

Prior to each pilot plant run, operating parameters were chosen and the condition to be evaluated discussed with the project officer and consultants. The pilot plant was then set up and allowed at least one day to stabilize prior to collecting samples. Chemicals to be fed were mixed in batch volumes and concentrations such that solutions could be prepared once each day for uninterrupted operation. Polymer solutions were prepared at solution strengths which would provide adequate dilution at the feed point. Two laboratory technicians were responsible for pilot plant operation and sample collection throughout the project.

As in any pilot plant operation, chemical feed pump problems and other miscellaneous mechanical problems often developed. In these areas and in pilot plant set-up and clean-up, plant personnel from the Ralph F. Brennan Plant provided invaluable assistance. In all conditions, samples to be analyzed for purposes of this study were only collected when there was continuous trouble-free operation for a suitable time (based on retention times of the pilot plant) prior to sample collection.

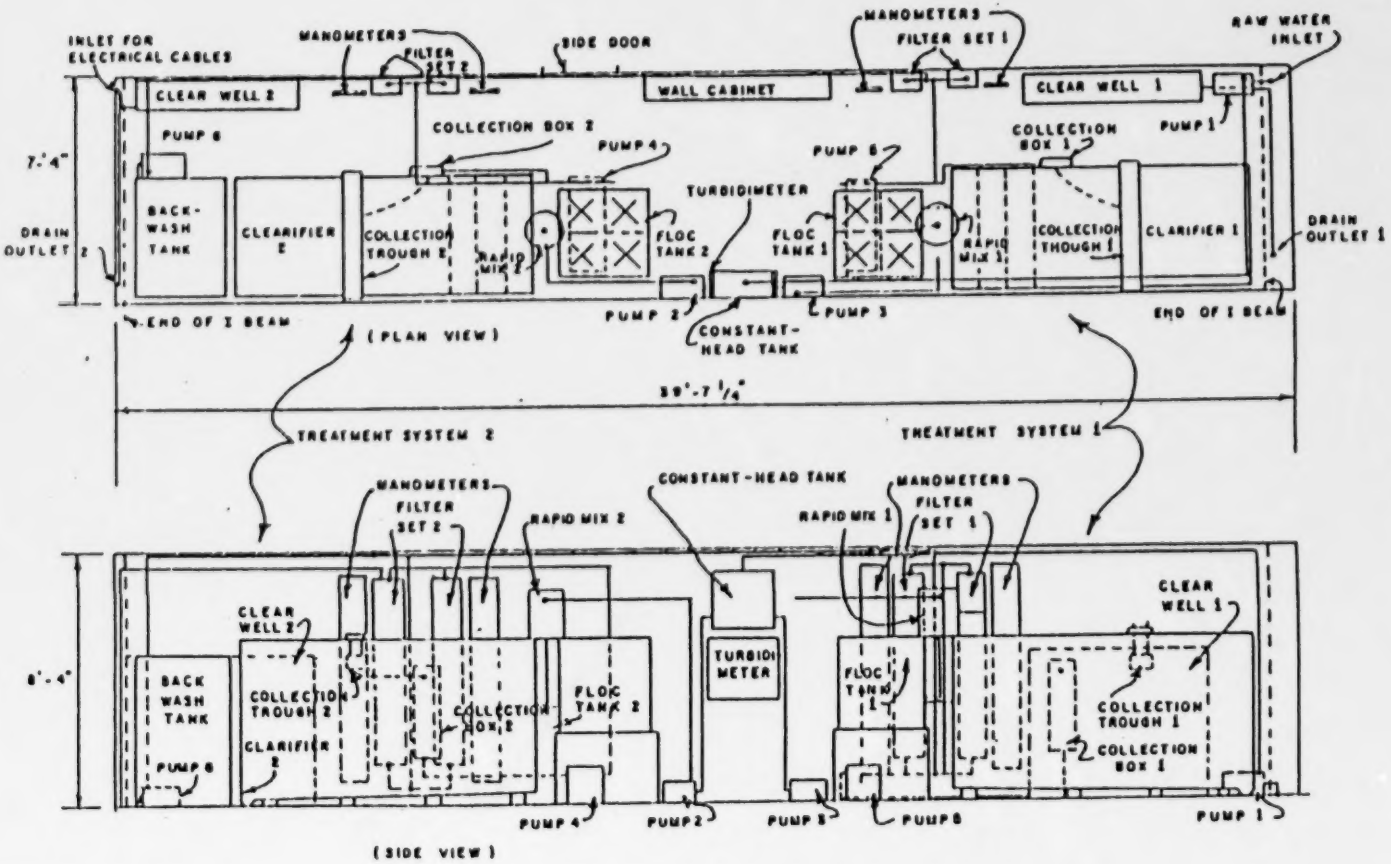


FIGURE 6 General layout of trailer-mounted pilot plant.

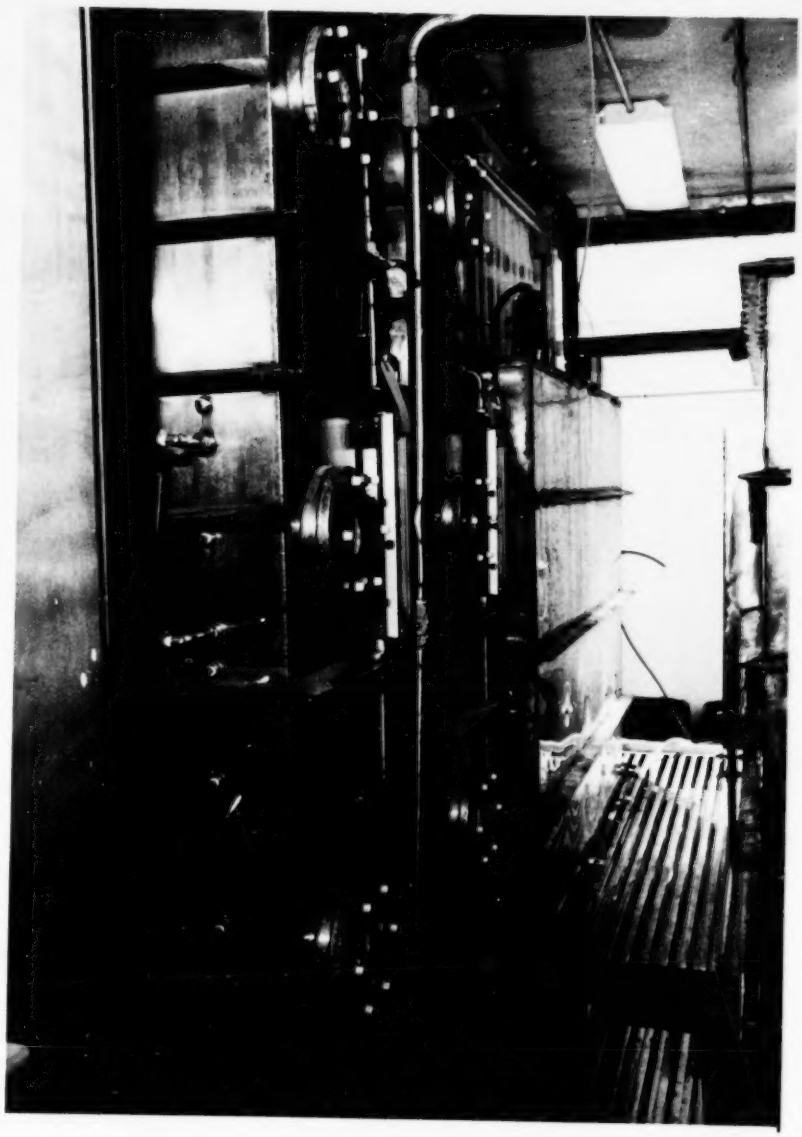


FIGURE 7 Interior of pilot plant.

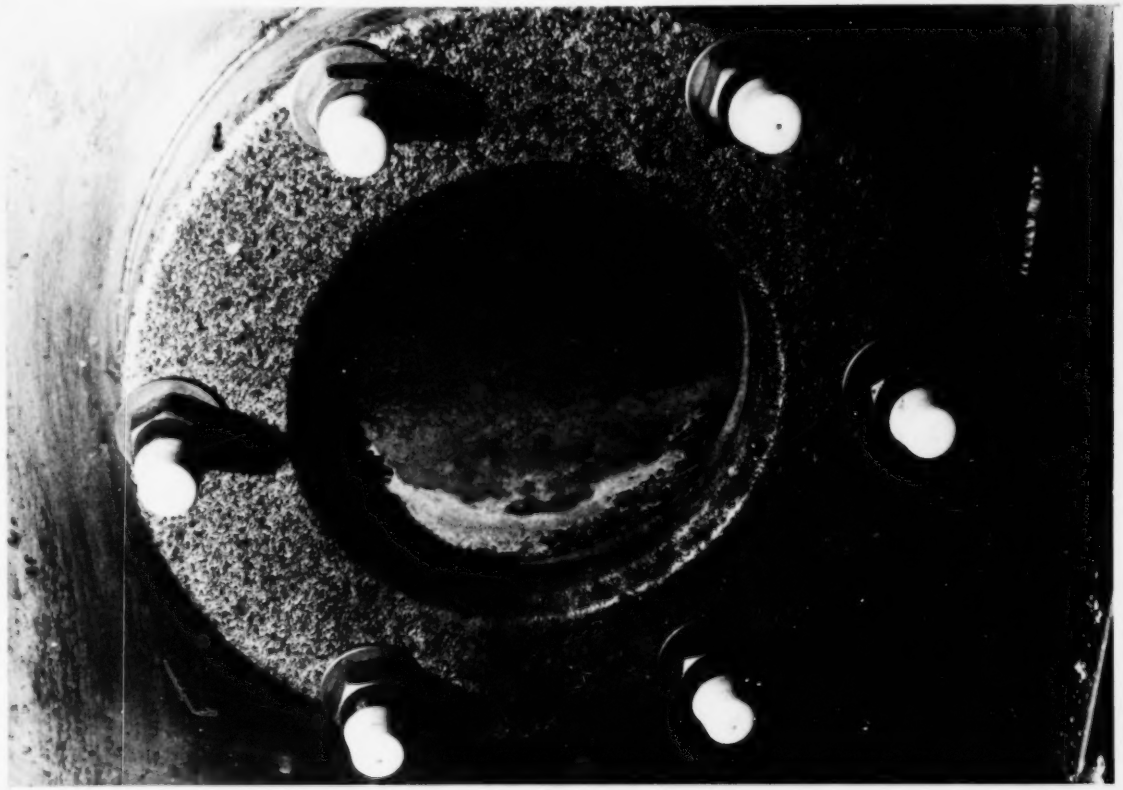


FIGURE 8 Pilot filter bed.

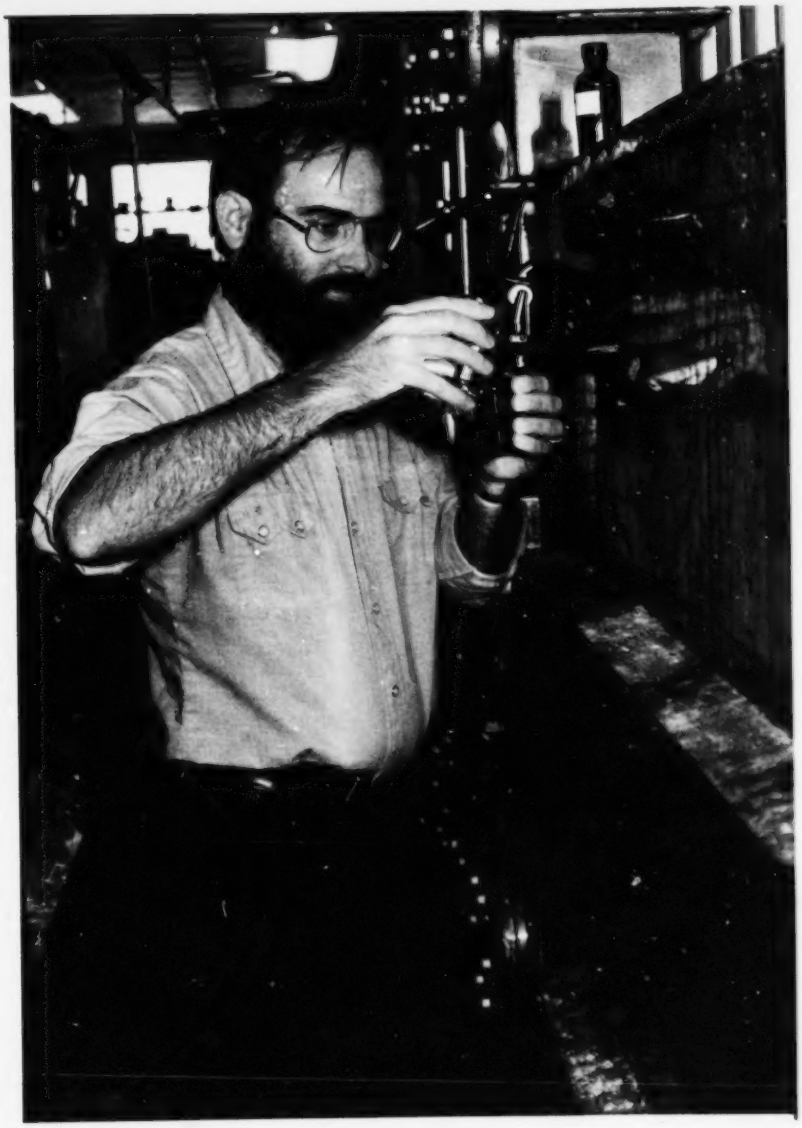


FIGURE 9 Collecting sample.

SECTION 7

DISCUSSION OF PILOT PLANT OPERATIONS

CONDITION #1

Condition 1 represented baseline conditions. The treatment scheme duplicated the Ralph F. Brennan Water Plant treatment process as nearly as possible. Essentially, treatment is a lime softening process with an anionic polymer addition to aid in flocculation. The condition was initiated May 22, 1981, and ran through to July 1, 1981. During the first period, only four sets of samples were collected due to operational problems. Because of this, Condition 1 was again set up in the pilot plant and run from November 20, 1981, to November 25, 1981, (referred to as condition 1-A.)

Condition 1 was set up as follows: Raw water was treated at a flow rate of .32 lps (5.0 gpm). Nalco 8184 anionic polyelectrolyte was introduced into the raw water immediately after the Corad water meter at a dose of 0.6 mg/l. Injecting the polymer at this point allowed for complete dispersion prior to the floc tanks. Anhydrous calcium oxide (quicklime) was slaked and added to Floc Tank 1 where a rapid mixing occurred. Floc Tanks 2, 3, and 4 mixing speeds were sequentially tapered to allow for flocculation. The lime dose averaged 220 mg/L with adjustments made to maintain a pH of 9.3 in the clarifier effluent. Two mixed media filters were in operation with a combined flow of .32 lps (5.0 gpm.) A chlorine dose of 11 mg/L was injected into the clarifier effluent with adjustments made to maintain a 3.0 mg/L free chlorine residual in the finished water. This was the only pilot plant run where chlorine was added prior to filtration.

Operational problems centered around the lime feed system. Utilizing the rapid mix chamber as the point of addition proved to be impossible due to piping arrangements in the plant. Throughout the study, constant attention to the lime feed system was necessary to maintain the desired pH.

CONDITION #2

Condition #2 involved the use of a bentonite clay in conjunction with a cationic polymer. Run time was from July 2, 1981, to July 12, 1981. Ten sets of samples were collected and analyzed for THMs.

Condition 2 was set up as follows: Raw water was treated at a rate of .32 lps (5.0 gpm.) 1 mg/l clay was injected into the raw water immediately

FIGURE 10 Checking floc formation.

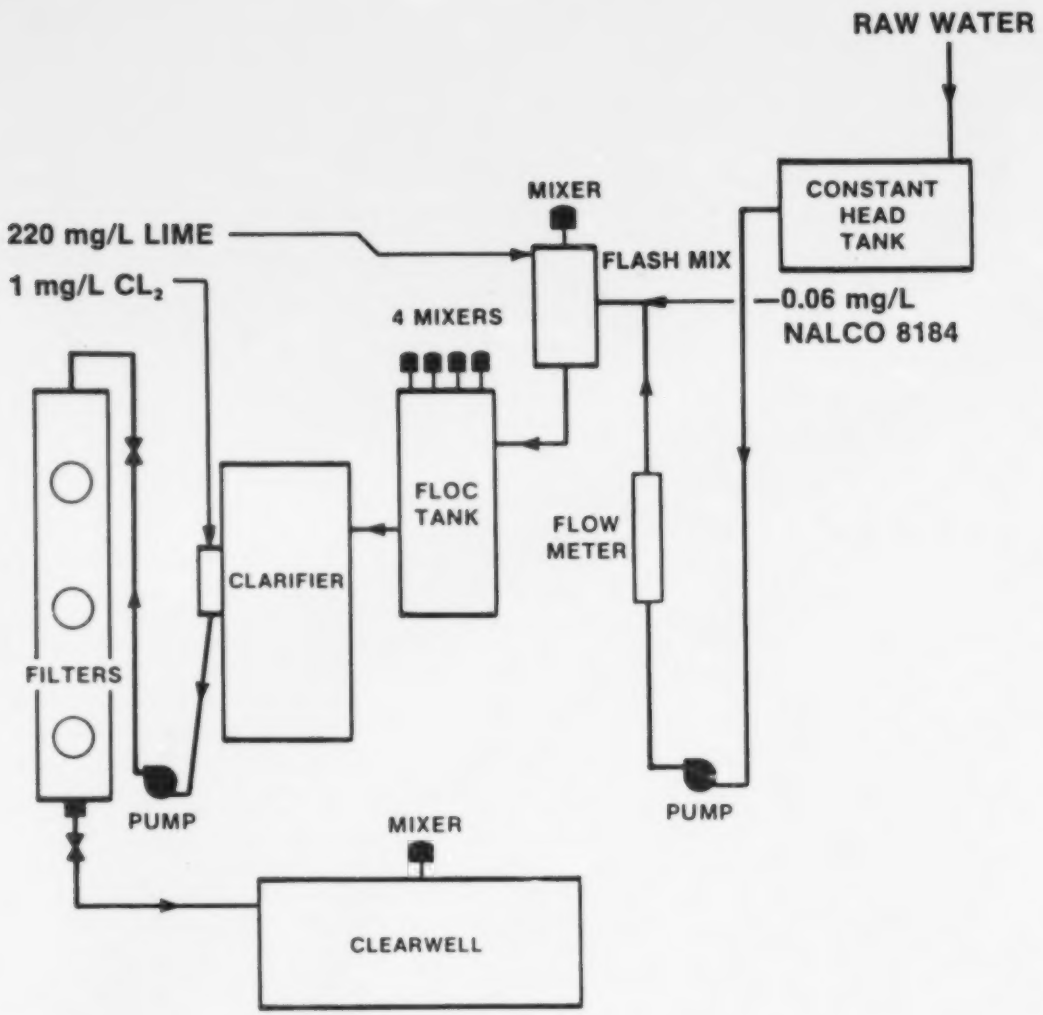


FIGURE 11 Pilot run no. 1.

after the constant head tank, allowing adequate time for the adsorptive abilities of the clay to take place. A cationic polymer was added at a dose of 1 mg/L just ahead of the rapid mix tank to ensure complete dispersal. Quicklime was slaked and pumped to Floc Tank 1 at an average dose of 220 mg/L. Adjustments were made to maintain a pH of 9.3 in the clarifier. Mixing speeds in Floc Tanks #2, #3, and #4 were tapered, respectively, to allow for good floc formation. Both filters were in operation with a combined flow of .32 lps (5.0 gpm.) Chlorination took place in the clearwell with adjustments made to maintain a chlorine residual of 3.0 mg/l in the finished water.

The clay required continuous mixing to remain in suspension; even so, problems developed from the clay settling in the discharge tubing and affecting the feed rate.

Filter runs averaged four days between backwashings.

CONDITIONS #3 and #4

Conditions #3 and #4 dealt with the use of alum as a coagulant in conjunction with the lime softening process. Condition #3 was initiated July 20, 1981, and ended July 30, 1981, followed by an immediate start-up of Condition #4 which lasted until August 2, 1981. Ten sets of samples for THMs were analyzed during Condition 3, while four sets were collected and analyzed from Condition #4 before sludge build-up problems in the pilot plant necessitated a shut-down and thorough cleaning.

The process design was identical in Conditions #3 and #4--only the dose of the coagulant differed. Liquid alum was fed to Floc Tank 1 (Conditions #3 at 20 mg/l and Condition #4 at 40 mg/l) where a rapid mixing occurred to ensure complete dispersion. Slaked lime and a non-ionic polymer, Magnifloc 985N, were added simultaneously to Floc Tank #2. The Magnifloc 985N, was fed at a dose rate of 0.3 mg/L. Slaked lime averaged a 220 mg/L dose rate with routine adjustments to maintain a 9.3 pH in the clarifier. Floc Tanks #2, #3, and #4 mixing speeds were tapered, respectively, encouraging optimum flocculation. Both filters were in operation with the combined flow at .32 lps (5.0 gpm.)

A chlorine solution was injected into the clearwell and adjustments made to maintain a free chlorine residual of 3.0 mg/l in the finished water.

During Conditions #3 and #4, several difficulties developed from the chlorine feed system which proved to be quite time-consuming. Filter runs remained at a four day average before loss of flow required backwashing.

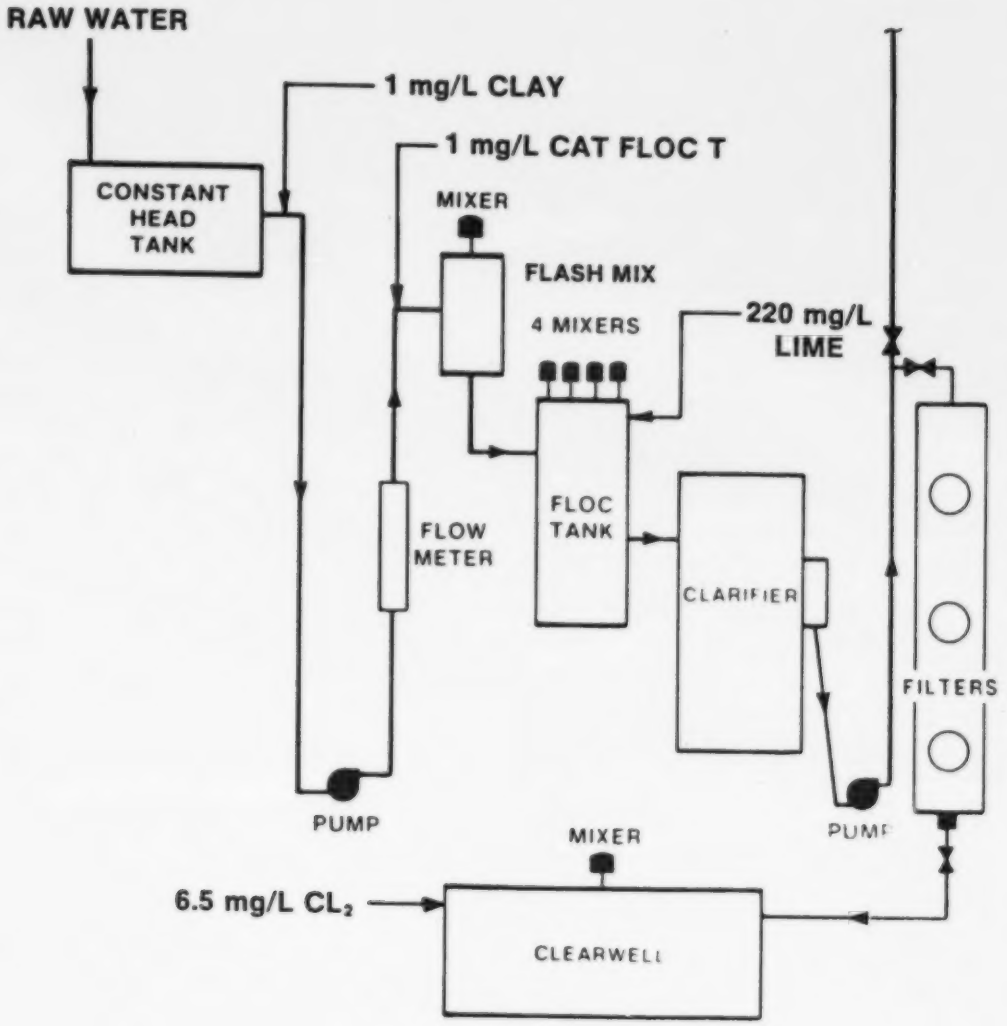


FIGURE 12 Pilot run no. 2.

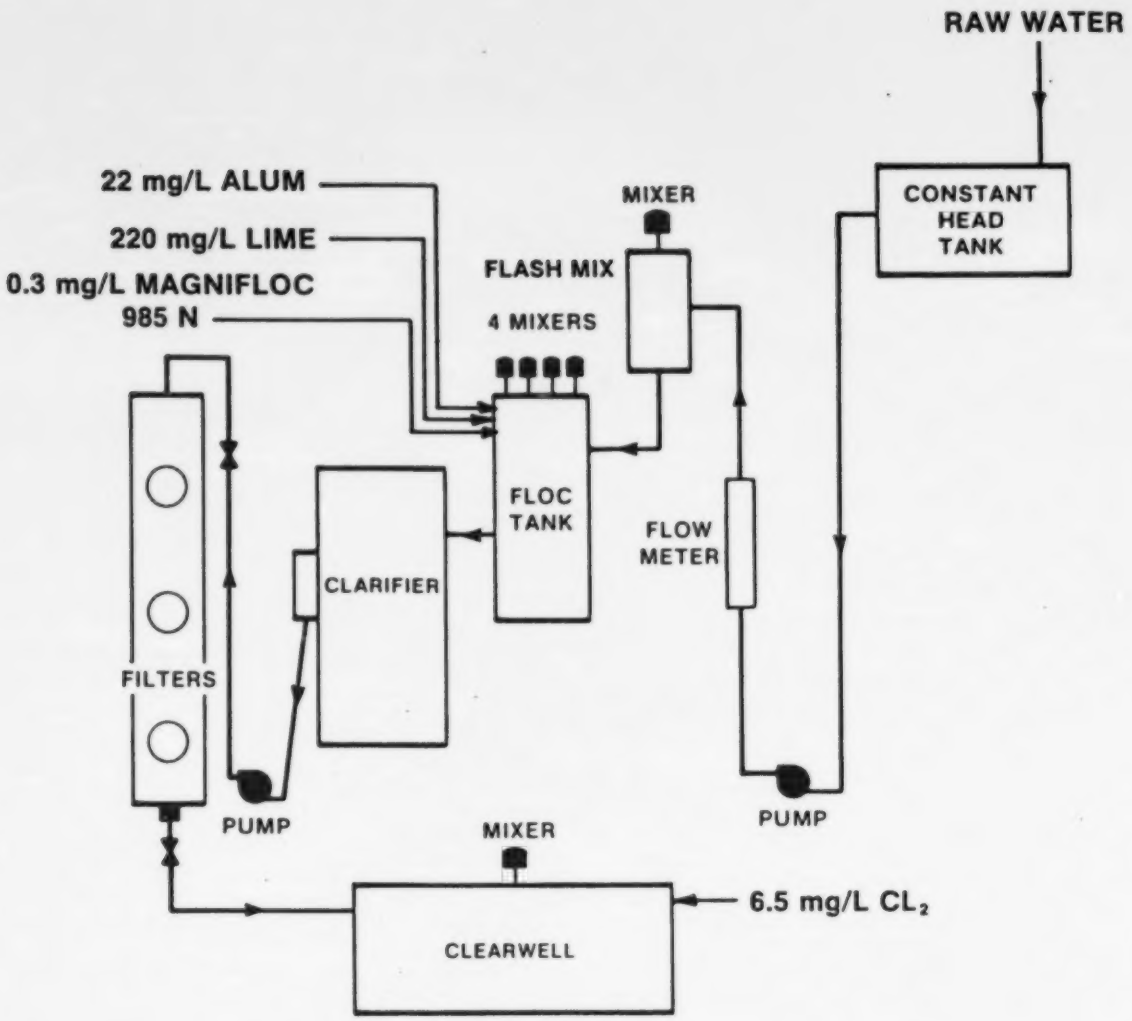


FIGURE 13 Pilot run no. 3.

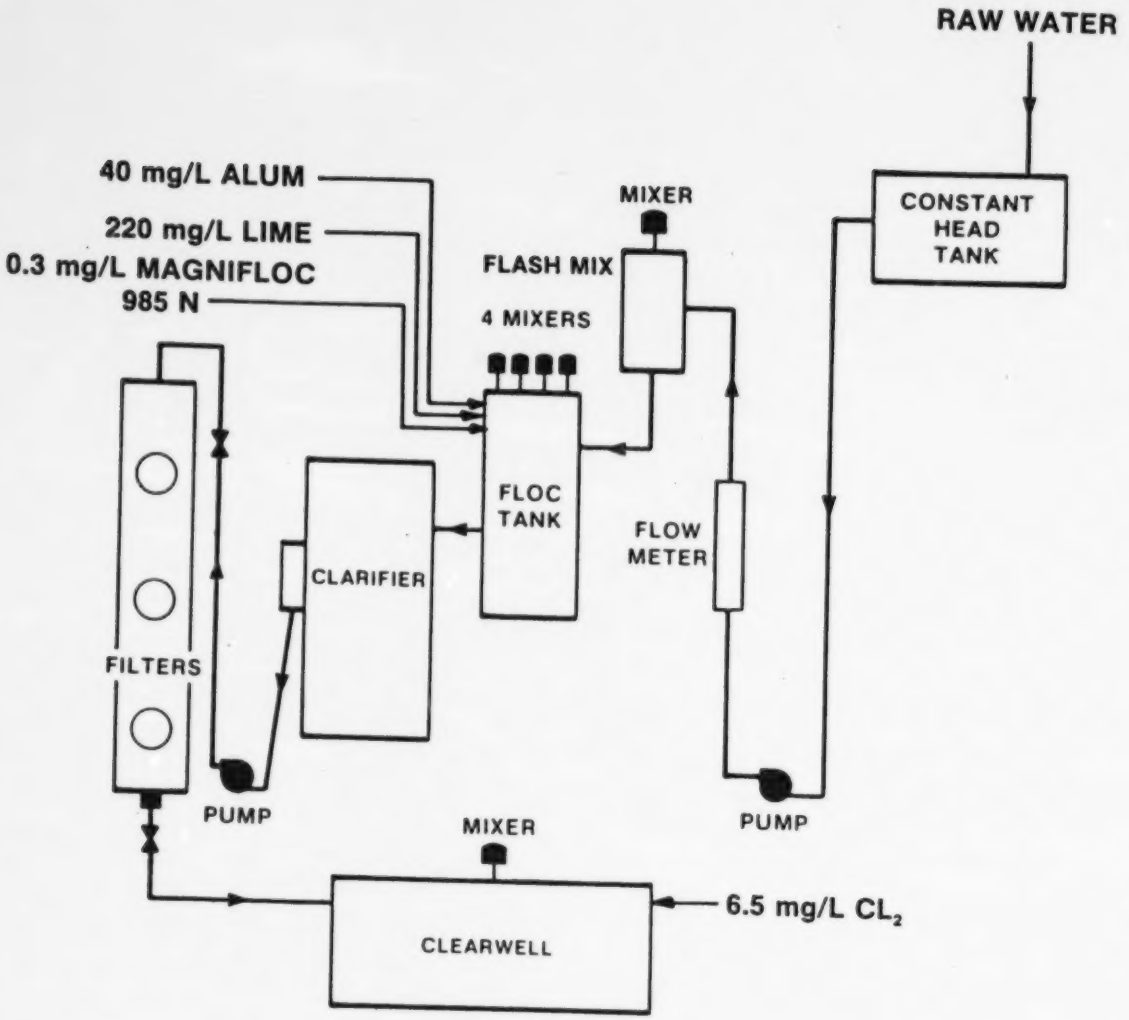


FIGURE 14 Pilot run no. 4.

CONDITION #5

Condition #5 involved the operation of both halves of the pilot plant in series. The process scheme was low pH coagulation followed by high pH softening.

Condition #5 ran from August 6, 1981 - August 24, 1981. Eight sets of samples were collected and analyzed for THMs. In addition to the raw and finished water samples, alum clarifier effluent samples were collected, chlorinated, stored for 3 days, and analyzed for THMs to evaluate precursor removal by the alum.

The physical set-up was as follows:

Raw water entered pilot Plant side #1 at a flow rate of 32 Lpm (18.9 gpm) Sulfuric acid was added to floc Tank #1 to drop the pH to 5.0. Liquid alum was injected into floc Tank #2 at a dose of 40 mg/L. Floc Tanks #1 and #2 were set at a rapid mixing speed. Floc Tanks #3 and #4 were tapered respectively for floc formation. The effluent from the clarifier in Plant #1 entered Plant #2 (plant configuration did not allow filtration prior to entering plant #2) at the rapid mix tank. Slaked lime was added at an average dose of 220 mg/L to floc Tank #1 where rapid mixing occurred. Floc Tanks #2, #3, and #4 mixing speeds were tapered for floc formation. Adjustments were made to the lime feed to maintain a pH 9.3 in the clarifier.

Both filters in Plant #2 were operational with a combined flow of .32 lps. Chlorination took place in the clearwell at a dose sufficient to maintain a 3.0 mg/L free chlorine residual.

Filter backwashing was necessary every four days.

During this study unusually high hardness concentrations were noted in the finished water. First thoughts attributed the additional hardness to the H_2SO_4 dissolving the $CaCO_3$ adhering to the walls of the floc tanks. However, jar testing indicated this not to be the case. The results of the jar tests indicate that additional hardness develops in the softening process. Increased alum doses and lime doses caused an increase in hardness. Taking into consideration the low alkalinities in Condition #5, this hardness appeared to be non-carbonate hardness, perhaps $CaSO_4$. To seriously consider this process scheme, the problem of non-carbonate hardness would have to be addressed by using recarbonation or substituting a different acid to lower coagulation pH or adding soda ash to remove the non-carbonate hardness.

Condition #5 also exhibited a foam over the surface of the alum clarifier. This foam was of a greenish-brown nature and did not seem to impart any taste or odor to the water.

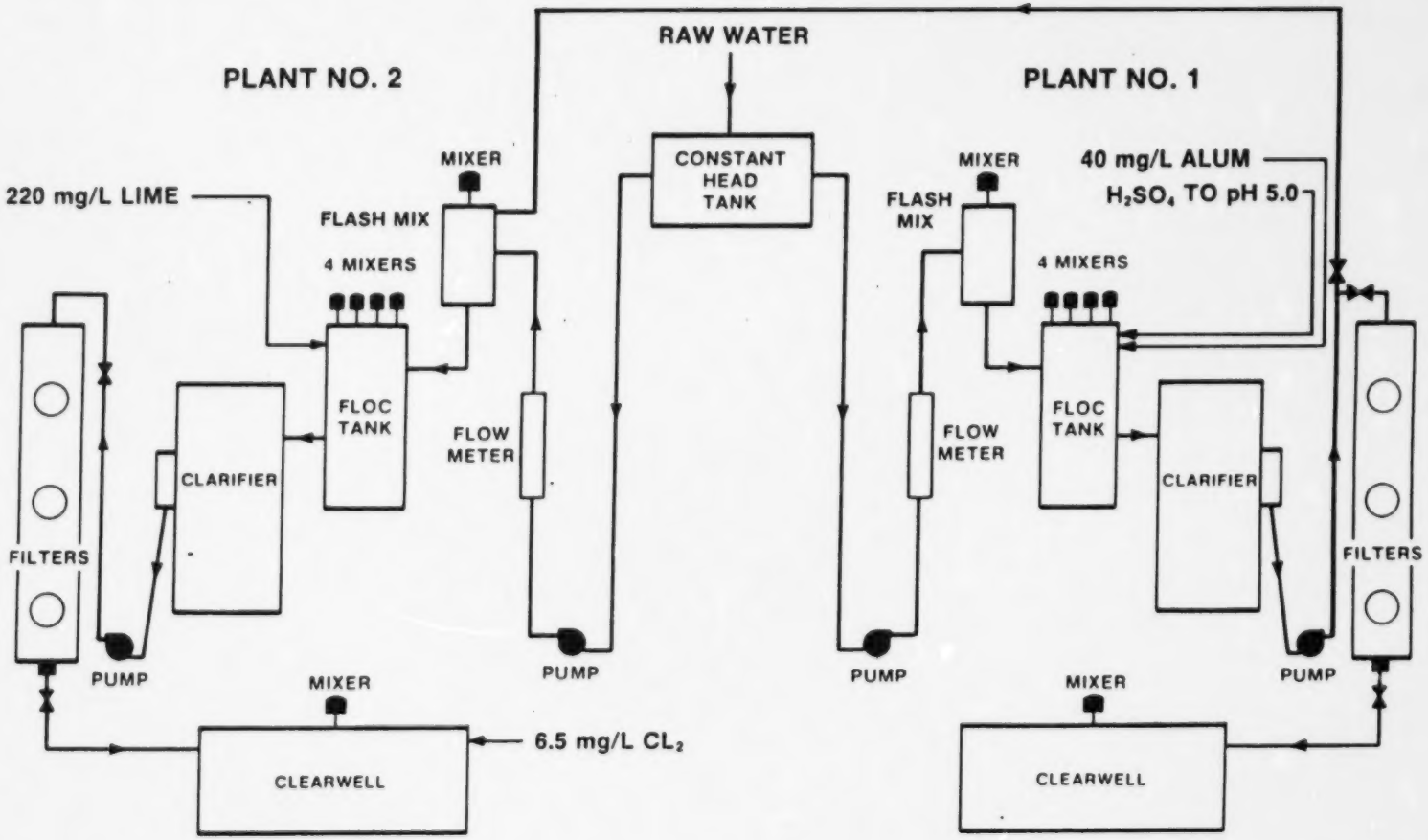


FIGURE 15 Pilot run no. 5.

CONDITION #6

Condition #6 involved the operation of both treatment plants in series. The process design was identical to Condition #5 with the exception of the alum dose which was increased from 40 mg/l to 80 mg/l. Condition #6 ran from September 1 to September 18, 1981. During this period, eleven sets of samples were collected and analyzed for THMs. In addition to the raw and finished samples, alum clarifier samples were collected, chlorinated, stored for three days, and analyzed for THMs.

Treatment design was as follows: Raw water was treated at a rate of 18.9 lpm. Sulfuric acid was added to the raw water in floc Tank #1 to drop the pH to 5.0-5.5. Liquid alum was injected into floc Tank #2 at a dose of 80 mg/L. Floc Tanks #1 and #2 were set at rapid mixing speeds. Floc Tanks #3 and #4 were tapered for floc formation. The coagulated water was allowed to settle with the clarifier effluent entering the rapid mix tank of the second plant. Slaked lime was added to floc tank #1 (Plant #2) at a dose of 220 mg/L. Floc Tanks #2, #3, and #4 mixing speeds were tapered, respectively. Adjustments were made to maintain a pH 9.3 in the final clarifier. Two filters were in operation with a combined flow of .32 lps. Chlorination took place in the clearwell to produce a 3.0 mg/L free chlorine residual.

Filter backwashing was necessary approximately every four days.

Condition #6 exhibited the same increase in finished water hardness as did Condition #5.

CONDITION #7

Condition #7 represented the reverse of Conditions #5 and #6. Raw water was lime-softened at a high pH followed by coagulation with alum.

This condition ran from September 28, to October 19, 1981. Seven sets of samples were collected and analyzed for THMs. In addition to the routine samples, lime clarifier samples were collected, chlorinated, stored for three days, and analyzed for THMs.

The chemical points of addition and doses were as follows: Raw water entered Plant #1 at a flow of .32 lps. Nalco 8184 polyelectrolyte was added prior to the rapid mix tank at a dose of .06 mg/L. Slaked lime was added to floc Tank #1 at a dose of 220 mg/L. Floc Tank #1 was set at a rapid mixing speed with floc Tanks #2, #3, and #4 tapered, respectively. Adjustments to the lime feed were made routinely to maintain a 9.3 pH in the clarifier. Clarifier effluent entered Plant #2 at the rapid mix tank. A 50 mg/l alum dose was added to floc Tank #1. The addition of alum brought the pH for coagulation into the desired range of 7.5-8.0. Sulfuric acid was set-up for any necessary pH adjustments in case of plant upset, though routinely, it was not needed. Two filters were in operation producing a combined flow of .32lps. Chlorination and pH adjustment took place in the clearwell of Plant #2. Adjustments were made to the chlorine feed system to maintain a

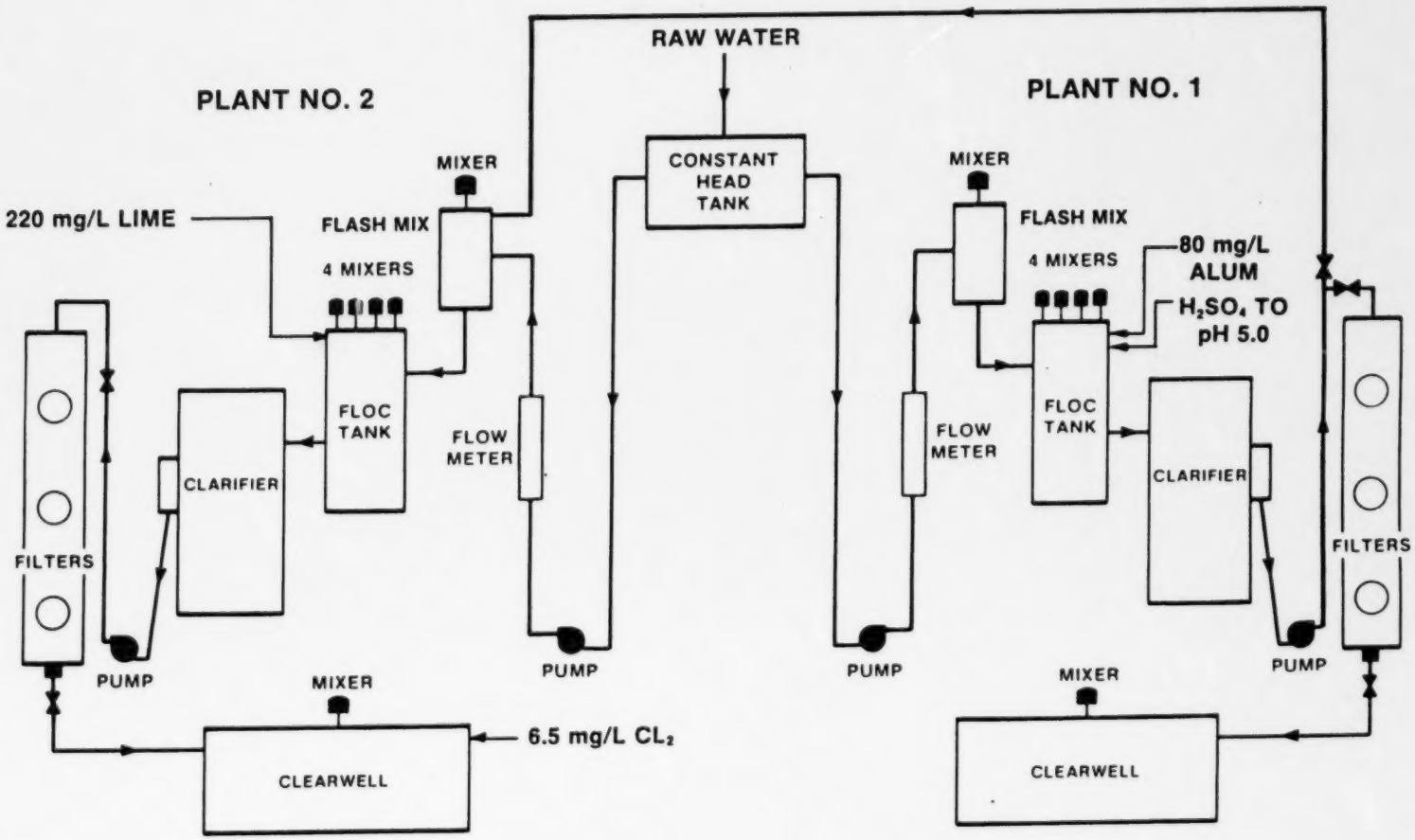


FIGURE 16 Pilot run no. 6.

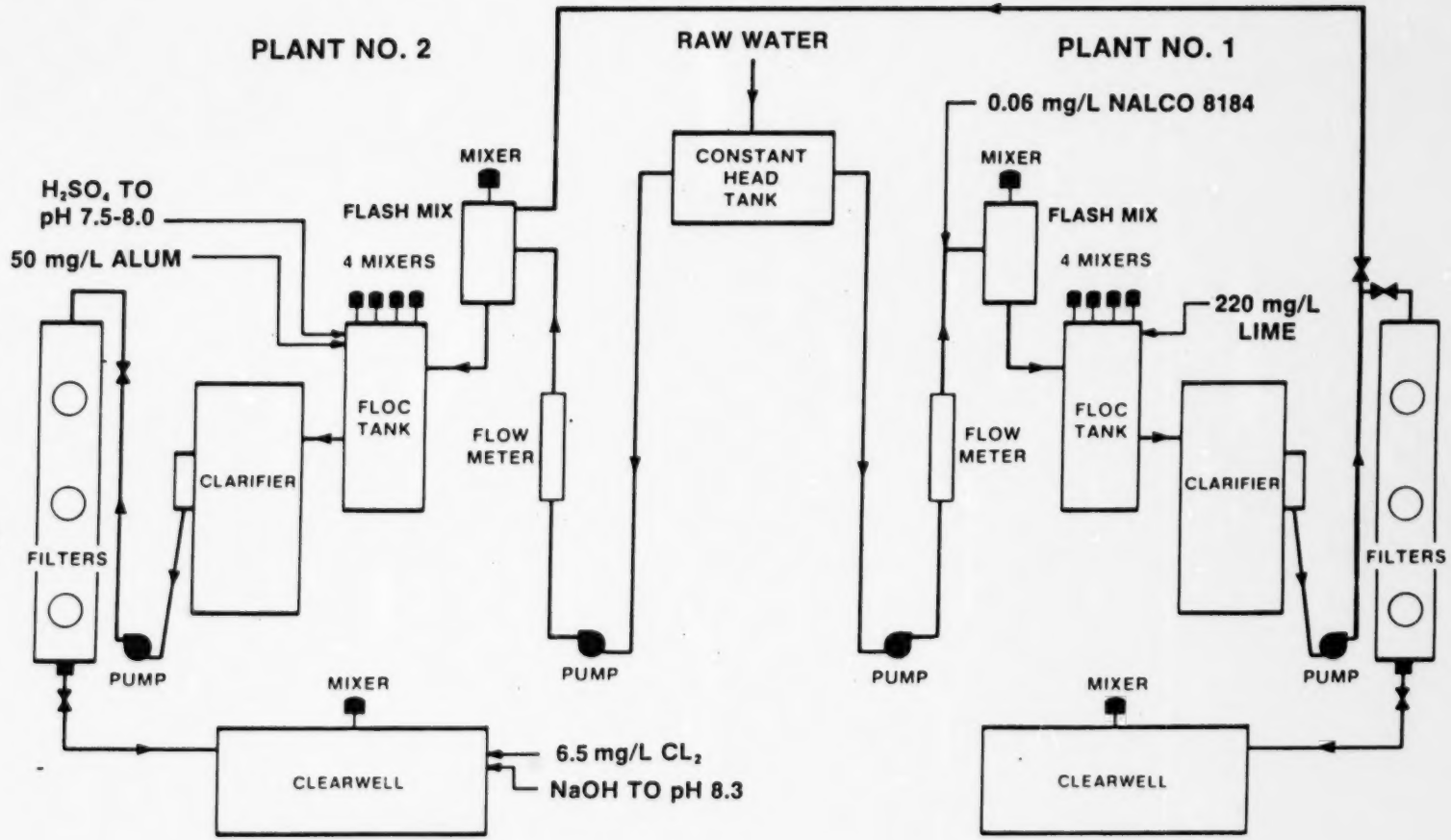


FIGURE 17 Pilot run no. 7.

3.0 mg/L free chlorine residual. Sodium hydroxide was added to raise the finished water pH to 8.3. The pHs for the Daytona Beach system is approximately 8.3, current practice is to maintain a final pH at or above pH 8.3.

This condition was extremely difficult to work with in the pilot plant. Five chemical feed systems were required to set-up the desired treatment plant design. The 8-10 hour detention time from the point of lime addition to the final effluent necessitated continuous monitoring of the softening pH in order to collect a representative continuous sample of finished water. Filter runs lasted only two days before backwashing was necessary. Turbidity carryover to the filter was very high during this condition resulting in some turbidity breakthrough and a final effluent of 10.1 NTU.

SUMMARY OF CONDITIONS #1 - #7

Condition #1 was extremely important to this study in that it established a base line from which we were able to compare alternate treatment schemes with respect to their precursor removal efficiencies. This treatment scheme has been developed over the past five years to optimize turbidity removal in the softening process and to maximize filter performance in a treatment process typical of that used in Florida precipitative softening plants. Data collected during this condition were compared with that from the Brennan Plant and with samples collected from the distribution system with respect to THM concentrations. As expected, reduction of formation potential through this treatment scheme was poor (less than 20% reduction), confirming the frequent observation that turbidity removal efficiency does not correlate well with THM precursor removal.

Pilot plant samples that were chlorinated and stored 72 hours generally produced higher THMs than Brennan Plant samples treated the same way (10% higher). This is most likely due to the higher efficiencies of the Brennan Plant's softening units which recirculate sludge produced internally and generally make more efficient use of chemicals than units where this recirculation is not practiced. Essentially, however, Brennan Plant conditions were simulated in the pilot plant with comparable results.

Condition #2 evaluated the use of a cationic polymer in conjunction with a bentonite clay. A slight improvement over the base line condition was noted; however, it was not determined conclusively whether this could be attributed to the coagulant or to the clay. Jar tests using clay alone suggest little if any potential for presursor removal.

Conditions #3 and #4 using alum as a primary coagulant in conjunction with lime softening showed only slightly better performance than that realized in Condition #2. Samples stored three days still produced THMs in excess of 300 ug/L.

Conditions #5 and #6 used alum again, but made use of pH adjustment prior to the alum addition and provided a settling step ahead of lime soften-

ing, making this a two-step coagulation process. Both of these conditions showed improved treatment with respect to THM formation, yet stored THMs were still more than twice the MCL. The intent of this treatment scheme was to first coagulate the precursor material and then remove it in a separate settling step prior to pH adjustment for softening; however, the extremely light floc produced did not settle well. High turbidities in the filter effluent were noted during this condition. This corresponded with large amounts of turbidity carry-over from the settling step of this treatment scheme.

To this point in the project, no treatment techniques were identified which would reduce precursor material enough to where, after chlorination and storage, THMs produced would be close to the 100 ug/L MCL.

CONDITION #8

In March 1980, a project was completed by the Rohm and Haas Company (under contract to EPA) involving the use of polymeric coagulants for THM precursor removal. The summary of this study[6] indicated that these coagulants could be quite effective in removing precursors from a number of different water sources. Of particular interest was that one of the waters treated in this study was a highly colored ground water collected from a south Florida water treatment plant. Although this water required the use of much higher doses than the other waters evaluated to reduce THM formation potentials to acceptable levels, the fact that this water was amenable to treatment by the coagulants indicated the potential for similar results using our own water source.

At the suggestion of the project officer, contact was made with Rohm and Haas, and a small amount of each coagulant (XE-392 and XE-391) was obtained for jar test work.

The jar test results indicated not only that these products could be effective in reducing THM formation potential, but that addition of a bentonite clay prior to any other chemical addition could enhance their performance considerably. More of the polymeric coagulant was supplied by Rohm and Haas, and the decision was made to pursue a pilot plant scale evaluation of its precursor removal capabilities.

Five mg/L of CA-35 (clay) was added in the form of a 1% slurry to the rapid mix tank, 20 mg/L XE-392 (6.5% stock slurry) to the first section of the floc tank, 3.5 mg/L XE-391 (10.7% stock slurry) to the second section, and the standard 220 mg/L of lime was added to the third section of the floc tank to maintain a pH of 9.4.

Due to the limited quantity of this new material available, the pilot plant was operated for eight hours each day for the first seven days of this condition rather than the usual continuous operation. For the final three days, we resumed 24-hour per day operation and reduced the XE-391 resin dose

to 2.5 mg/L. During this time, we saw a 14% decrease in THM formation over the previous seven days' operation.

This condition produced the lowest THMs to date. Seventy-two hour stored finished water samples averaged 158 ug/L THMs. The sludge formed during this condition was much darker than the off-white calcium carbonate sludge usually produced in our softeners and apparently contained much of the organic color which was removed from the water. During the trial, the settled water actually appeared blue rather than the green color previously observed, although this is not reflected in color measurements.

It was also noted that during this condition, filter runs were nearly twice as long as those of the previous conditon. This was quite surprising since the floc formed during this run was extremely light and fluffy and would have been expected to form a mat on the filter surface similar to alum sludge. Previous experience[6, 7, 8], has shown that alum/ $CaCO_3$ sludge penetrates mixed media filters poorly, leading to very short intervals between backwashing these filters.

Turbidity breakthrough of the filters may be a problem using this treatment scheme as evidenced by high effluent turbidities. However, it was not determined whether this was a function of particle size passing through the filters, of high turbidity loading of the filters caused by high carry-over from the settling tank or of inadequate flocculation of the XE-392.

COST ANALYSIS

In considering the relative merits of the treatment schemes evaluated in this study, cost figures in terms of cost per thousand gallons of water produced were derived for conditions 1 through 8. These figures (based on 1981 chemical costs and capital equipment costs where applicable) are presented in Table 8. In figure 26 average precent removal of precursor material as estimated from the equation:

$$\frac{RWSC - FWSC}{RWSC}$$

shows conditions 6 and 8 to be the most effective in terms of precursor material, yet they also are the most costly treatment methods evaluated. Condition 8 which came closest to the 100 ug/L goal for stored THM samples is nearly six times the treatment cost of condition 1, the current scheme used in the Ralph Brennan Water Plant. This is not to say, however, that a customer's water bill would be increased by the same factor if the scheme were used in a municipal plant since typically chemical costs are only a portion of the total cost of operation reflected in a customer's water bill.

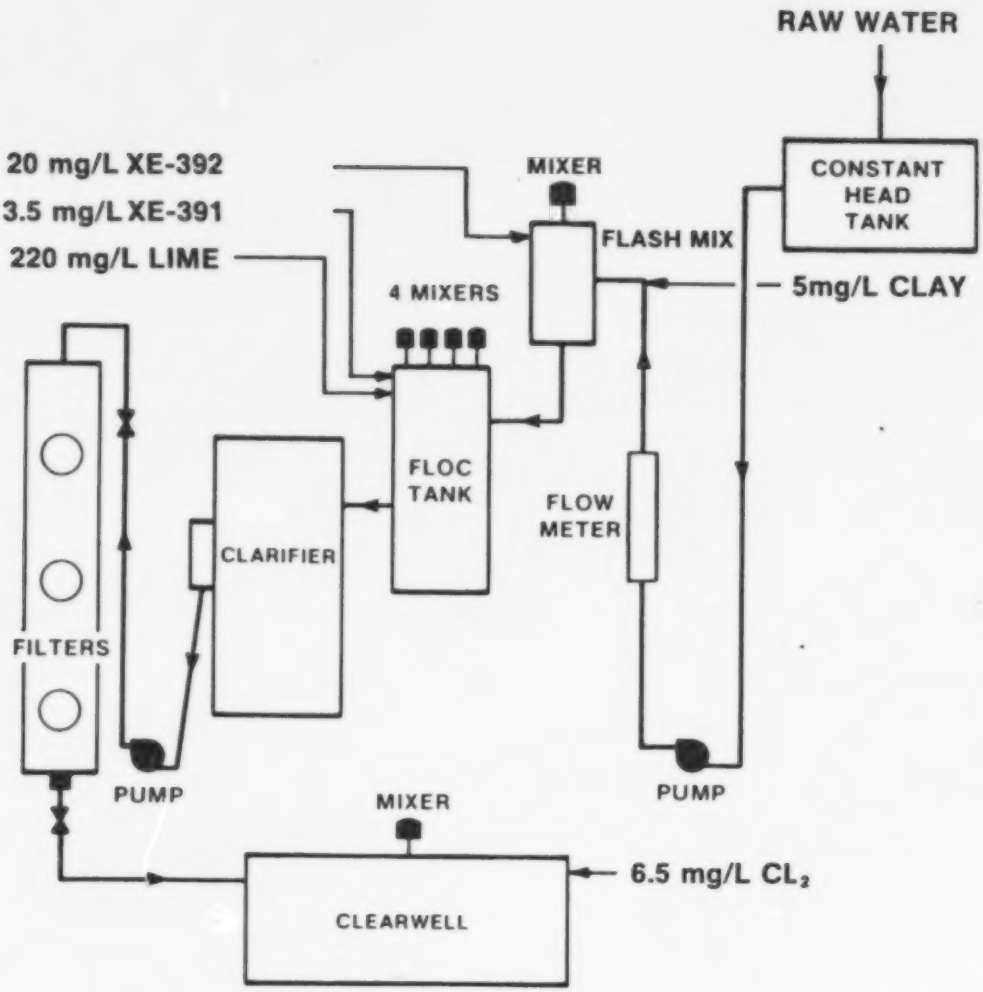


FIGURE 18 Pilot run no. 8.

TABLE 2. RAW WATER ANALYSIS DURING STUDY (AVERAGES)

Condition 1	pH	T.H. mg/l as $CaCO_3$	alk. mg/l as $CaCO_3$	turbidity NTU	color PCU
	6.9	294	0/264	4.2	17
Condition 2					
	7.0	332	0/250	65	25
Condition 3					
	7.1	400	0/236	13	18
Condition 4					
	NONE				
Condition 5					
	7.1	400	0/236	13	18
Condition 6					
	6.7	360	0/254	1	25
Condition 7					
	6.8	340	0/252	1	20
Condition 8					
	6.8	340	0/266	0.1	25

Raw water table showing consistency of Daytona Beach source water quality, with respect to pH, total hardness (TH), bicarbonate alkalinity (Alk) and color.

TABLE 3. CHLORINE DEMANDS (mg/L free residual*)
(Initial Dose 15 mg/L)

Condition	15 Minute Demand	30 Minute Demand	60 Minute Demand	1 Day Demand	2 Days Demand	3 Days Demand
1	6.1	6.2	6.5	11.2	12.5	13.3
2	5.6	5.9	6.3	3.8	11.9	12.4
3	5.9	6.4	7.4	11.2	12.5	13.4
4	5.8	6.7	6.8	10.7	12.0	12.5
5	8.0	8.4	8.4	11.5	12.4	12.9
6	7.9	7.9	7.9	10.8	11.6	12.5
7	1.6	1.6	2.5	6.0	6.6	7.6
8	4.0	4.2	4.3	5.9	6.8	7.4

Table of chlorine demands determined under each condition using product water dosed with chlorine.

TABLE 4. PILOT PLANT DAILY AVERAGE FINISHED WATER ANALYSIS

Condition	pH	P/M alk. as $CaCO_3$	Total Hardness mg/L as $CaCO_3$	Free Chlorine mg/L Residual	Color PCU	Turbidity NTU
1	8.9	5/63	126	3.1	6.2	0.2
1A	8.2	23/59	117	3.2	14	1.2
2	8.4	5/57	105	3.1	13	3.2
3	8.5	13/70	126	4.3	9	1.3
4	8.0	0/67	108	4.2	6	0.5
5	8.1	12/73	270	5.8	8	0.9
6	7.6	6/86	371	4.5	8	2.4
7	8.2	14/87	154	2.8	10	10.1
8*	7.8	13/89	129	3.8	9	8.7
8**	7.9	20/60	103	4.8	8	2.2

* 8-Hour Operation
** 24-Hour Operation and Lower XE-391 dose

TABLE 5. AVERAGE THM CONCENTRATION IN PILOT PLANT (ug/L)

	Cond.#1	Cond.#2	Cond.#3	Cond.#4	Cond.#5	Cond.#6	Cond.#7	Cond.#8	Cond.1-b
RW									
$CHCl_3$	1.14	.743	1.15	1.61	0.00*	0.00	0.00	0.00	0.00
$CHBrCL_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CHBr_2Cl$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CHBr_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TTHM	1.14	.743	1.15	1.61	0.00	0.00	0.00	0.00	0.00
RWSC									
$CHCl_3$	268	377	376	364	356	273	314	272	271
$CHBrCL_2$	81.4	75.3	76.8	61.7	73.5	56.3	58.6	57.5	56.3
$CHBr_2Cl$	11.0	7.77	8.37	6.66	8.76	6.78	7.43	8.38	34.7
$CHBr_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TTHM	360	460	461	432	438	336	380	338	362
FWID									
$CHCl_3$	51.0	41.8	44.0	54.4	36.7	31.4	41.6	21.1	66.3
$CHBrCL_2$	15.7	9.90	11.1	11.2	7.35	9.6	10.6	8.60	17.4
$CHBr_2Cl$	3.63	4.28	3.12	3.10	2.23	2.49	2.62	3.13	4.32
$CHBr_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TTHM	70.3	56.0	58.2	68.7	46.3	43.5	54.8	32.8	88.0
FWSC									
$CHCl_3$	249	262	248	238	219	155	203	98.3	226
$CHBrCL_2$	79.3	72.6	66.6	59.6	57.1	54.1	57.0	44.0	56.9
$CHBr_2Cl$	22.8	15.8	14.4	14.7	17.2	10.4	12.6	14.9	14.4
$CHBr_3$	0.00	.43	0.28	0.00	1.23	.234	0.0	0.831	0.00
TTHM	351	351	329	312	295	220	273	158	297
ACSC					ACSC	ACSC	LCSC		
$CHCl_3$					205	195	339		
$CHBrCL_2$					39.3	43.0	71.2		
$CHBr_2Cl$					4.66	5.80	13.4		
$CHBr_3$					0.00	0.00	0.00		
TTHM					249	244	424		

*Abbreviations:

0.00 - Below detection limits
LCSC - Lime clarifier, superchlorinated, stored 72 hours.
RW - Raw water
RWSC - Raw water, super chlorinated, stored 72 hours.
FWID - Finished water, immediately dechlorinated.
FWSC - Finished water, super chlorinated.
ACSC - Alum clarifier, super chlorinated, stored 72 hours.

TABLE 6. RELATIVE COST OF TREATMENT

Test Condition	Construction Requirements	Estimated Construction Cost	Chemical Costs per 1,000 Gal.										
			Lime	Cl_2	Alum	Ferric	Poly	Clay	Polymeric Coagulant	Base	Acid	Repumping	Total
1	None	N/A	.038	.092			.001						$0.131
2	None	N/A	.038	.054			.004	.001					$0.097
3	None	N/A	.038	.054	.019		.003						$0.114
4	None	N/A	.038	.054	.034		.003						$0.187
5	2 Clarifiers Repumping Facilities Misc. Piping	$210,000 $ 30,000 $ 20,000	.038	.054	.034						.008	0.400	$0.534**
6	2 Clarifiers Repumping Facilities Misc. Piping	$210,000 $ 30,000 $ 20,000	.038	.054	.068						.008	0.400	$0.568**
7	2 Clarifiers Repumping Facilities Misc. Piping	$210,000 $ 30,000 $ 20,000	.038	.054	.043		.001			.008	.008	0.400	$0.552**
8	None	N/A	.038	.054		.021		.005*	.636				$0.754

*Based upon estimated price of $2.00/lb for XE-391 and $6.00/lb for XE-392.

** Does not include amortized cost of new facilities or O&M cost of those facilities.

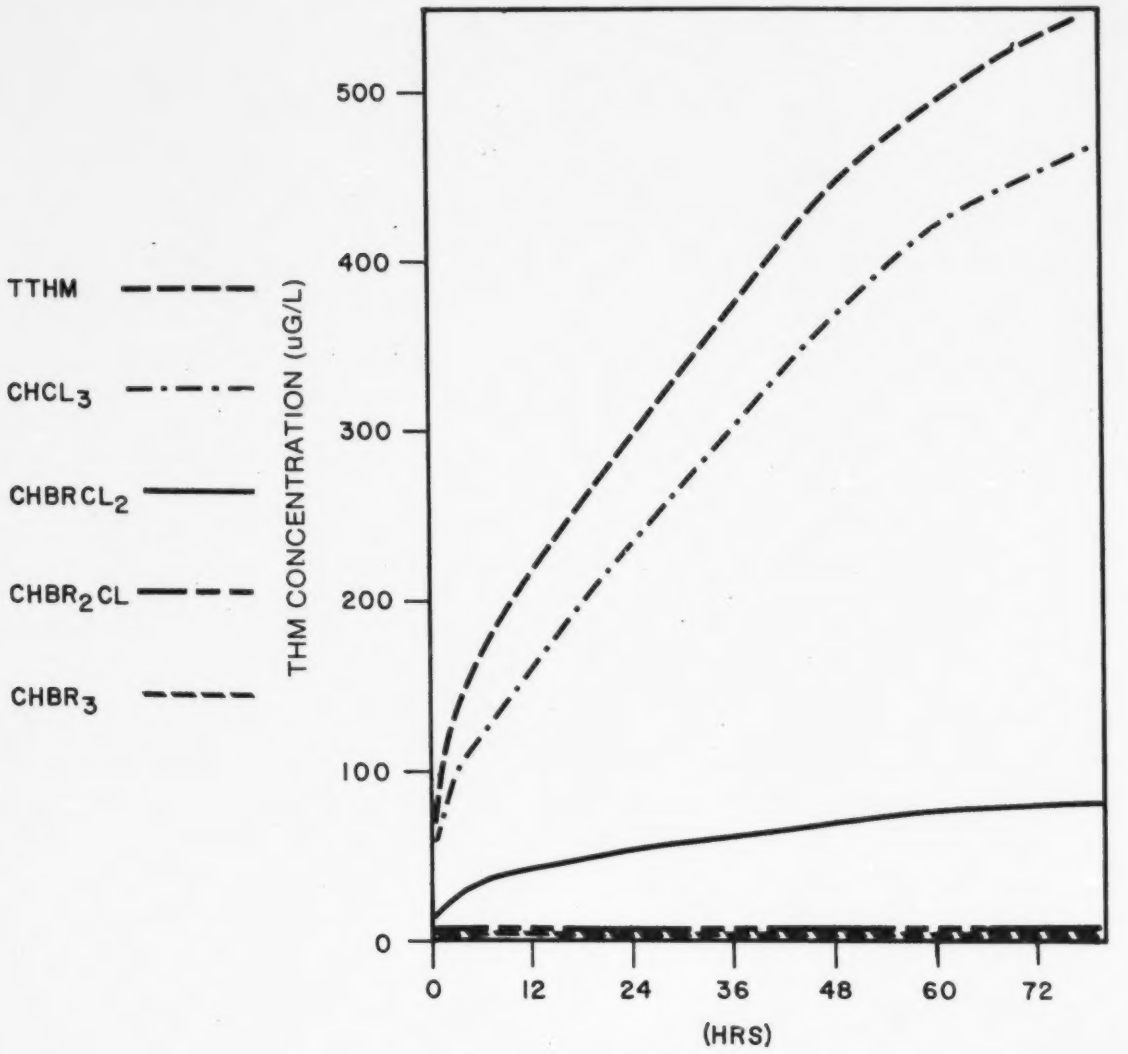
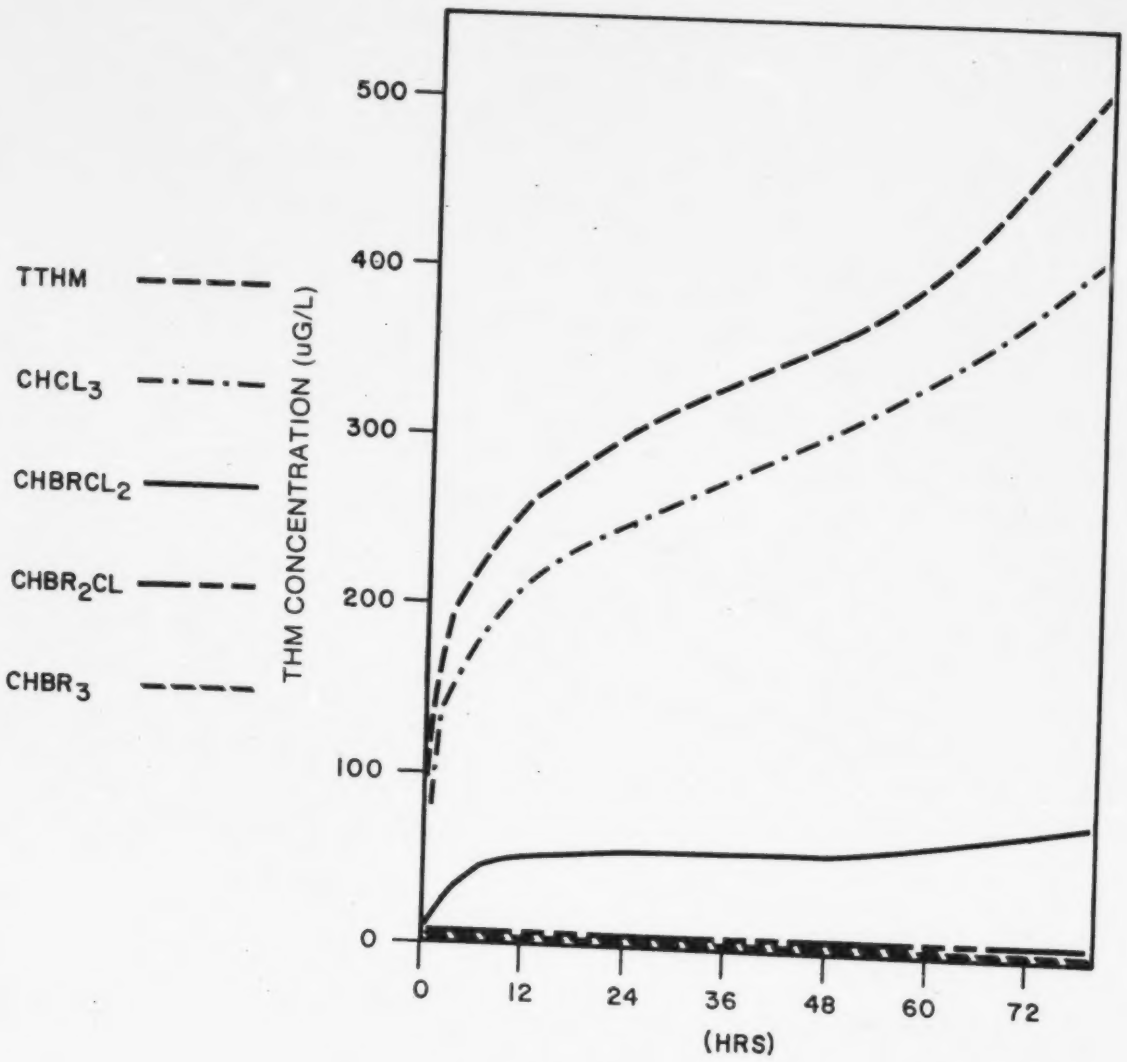


FIGURE 19 Time stored vs. THM concentration (26 Jul. 81).



TIME STORED PRIOR TO DECHLORINATION
(ALL SAMPLES RAW WATER DOSED WITH 27mg/L Cl_2).

RAW WATER THM FORMATION CURVES FOR DAYTONA BEACH SOURCE WATER

FIGURE 20 Time stored vs. THM concentration (18 Aug. 81).

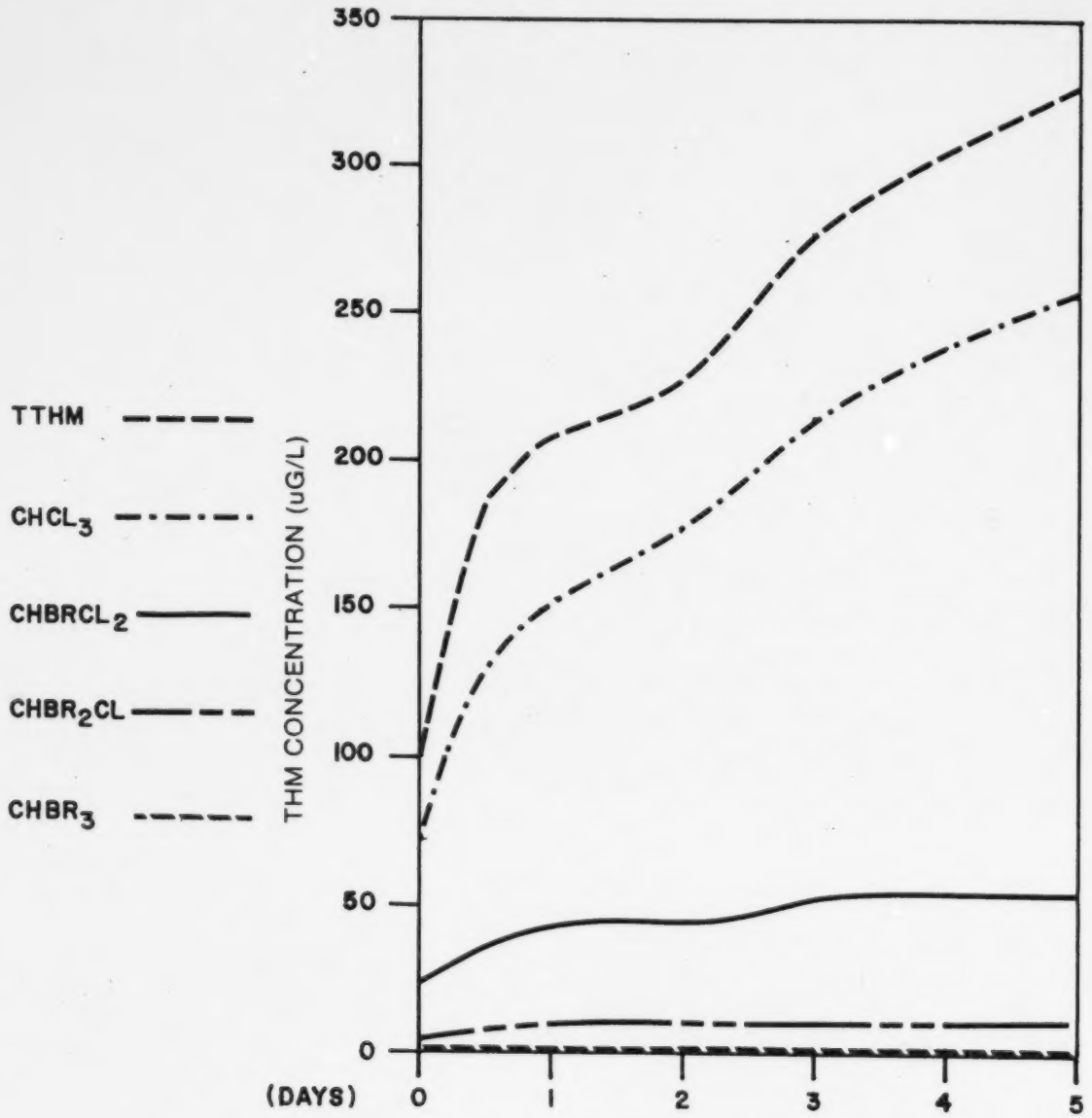
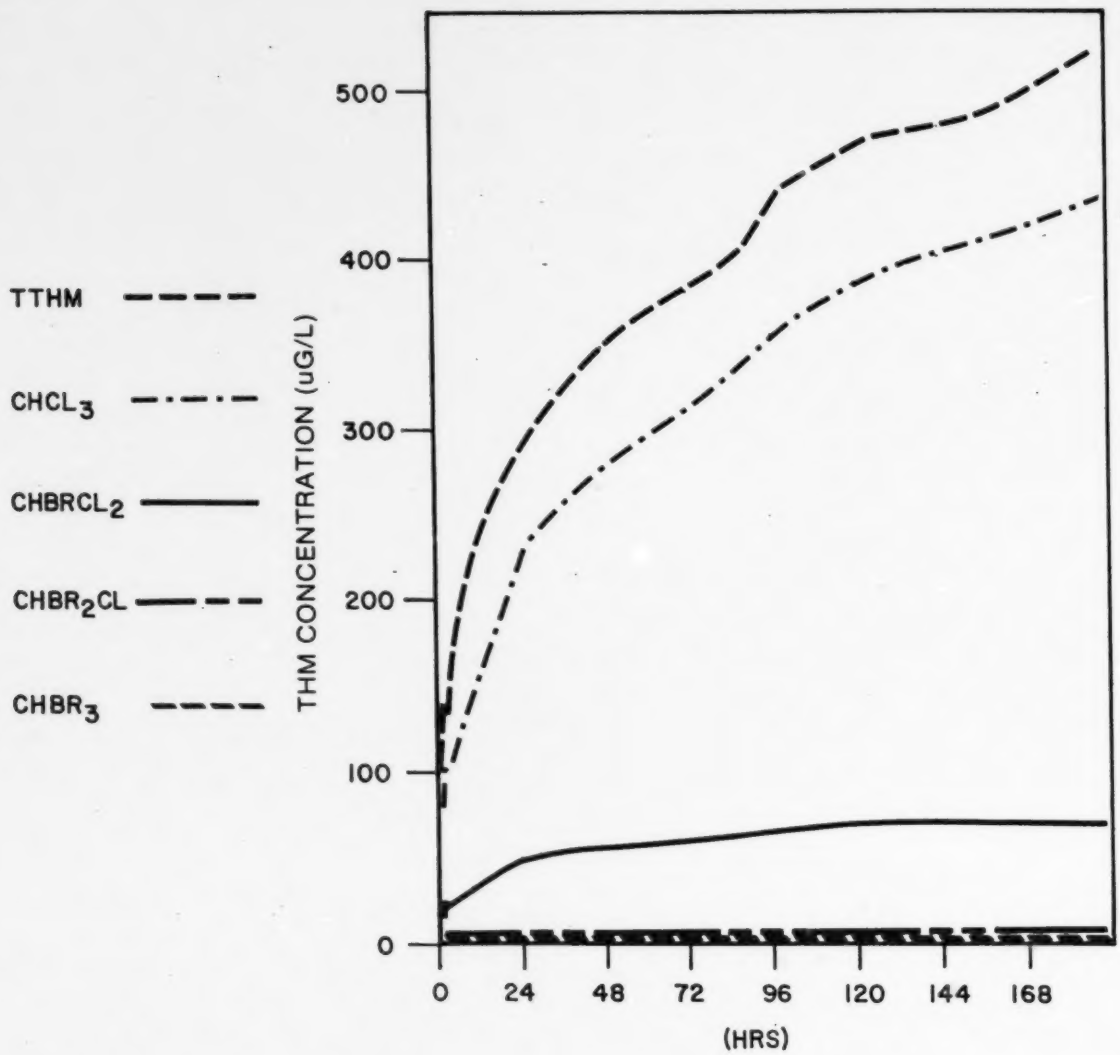
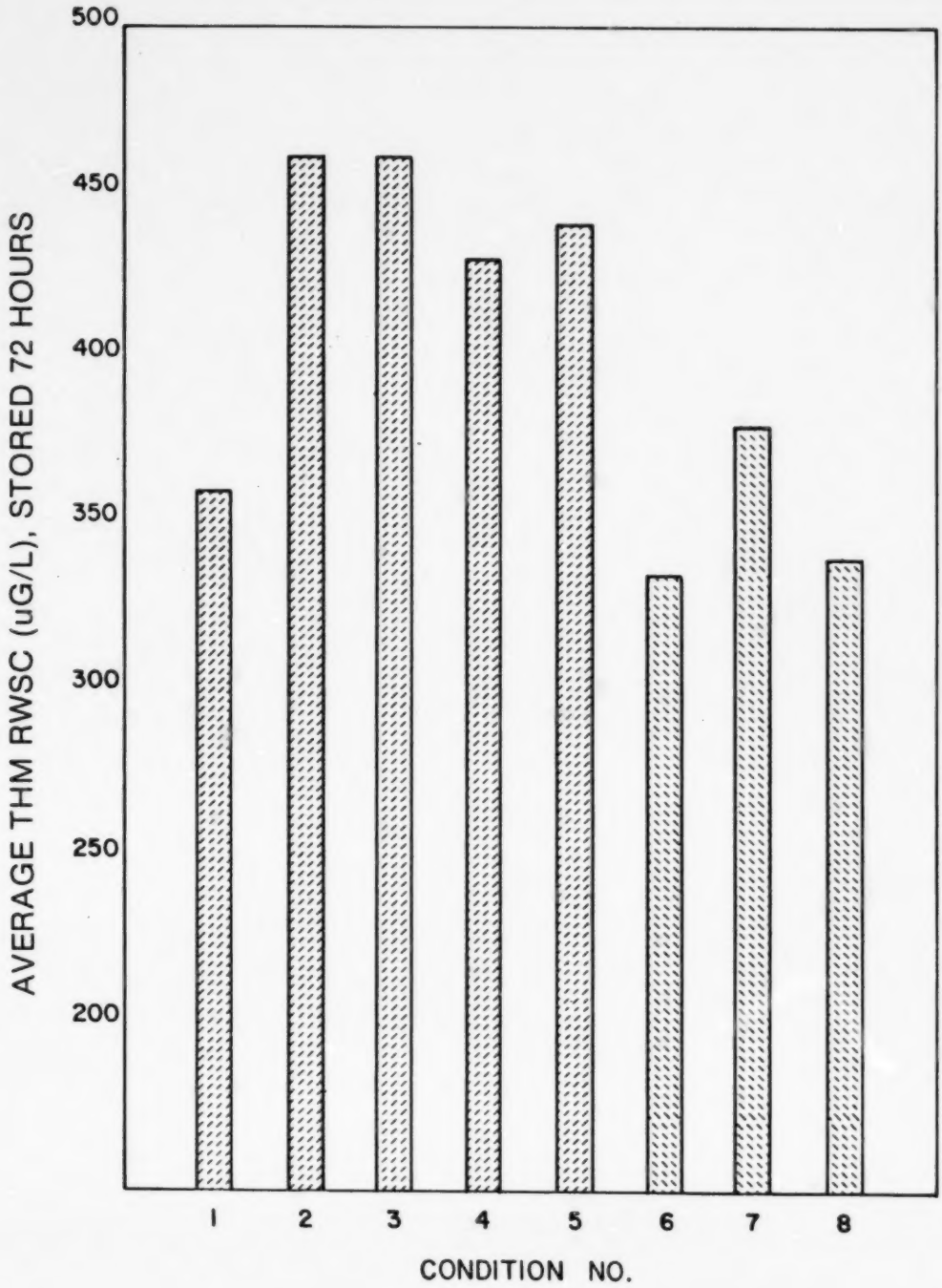


FIGURE 21 Time stored vs. THM concentration (9 Sept. 81).



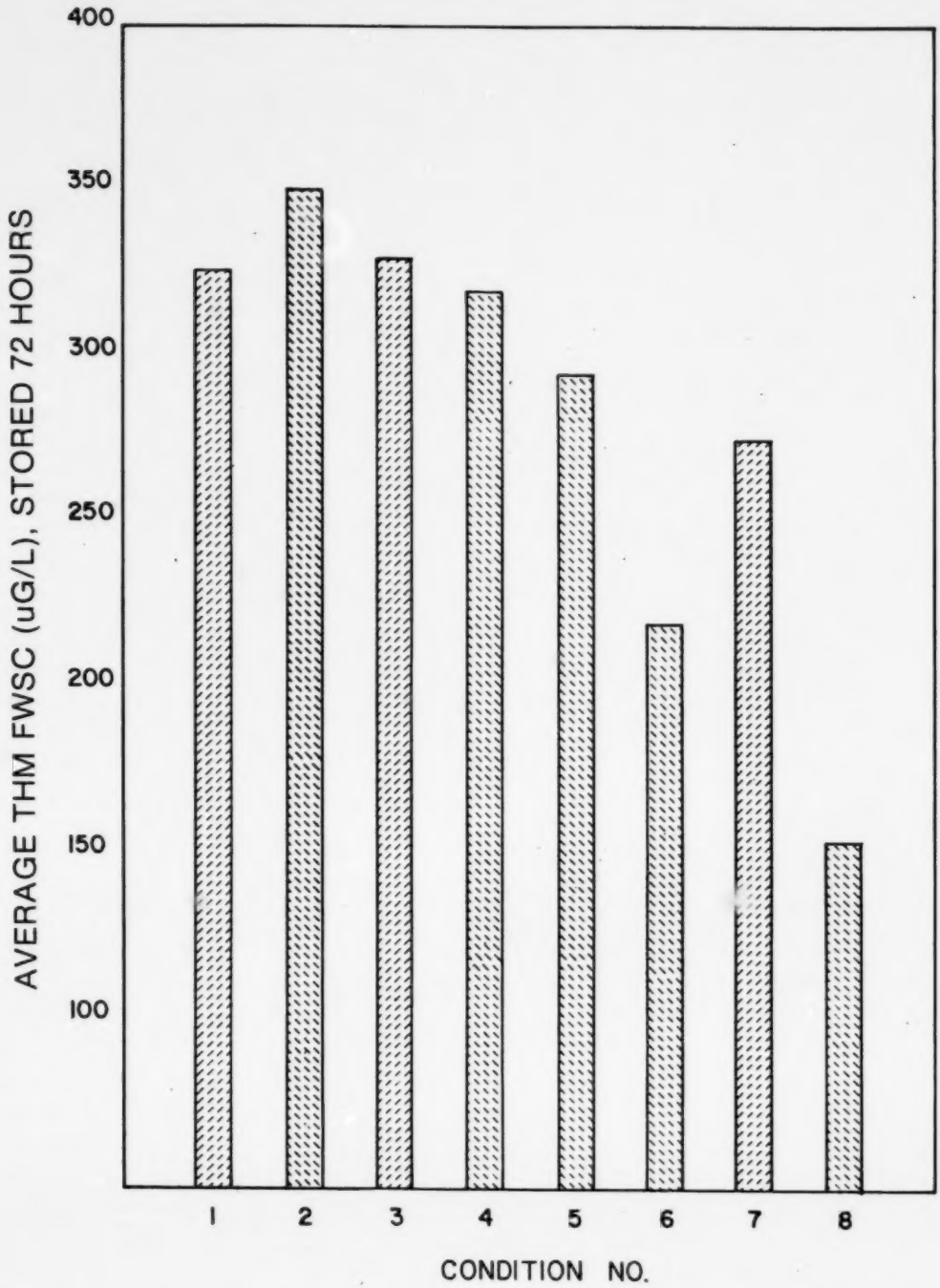
RAW WATER THM FORMATION CURVES FOR DAYTONA BEACH SOURCE WATER

FIGURE 22 Time stored vs. THM concentration (13 Oct. 81).



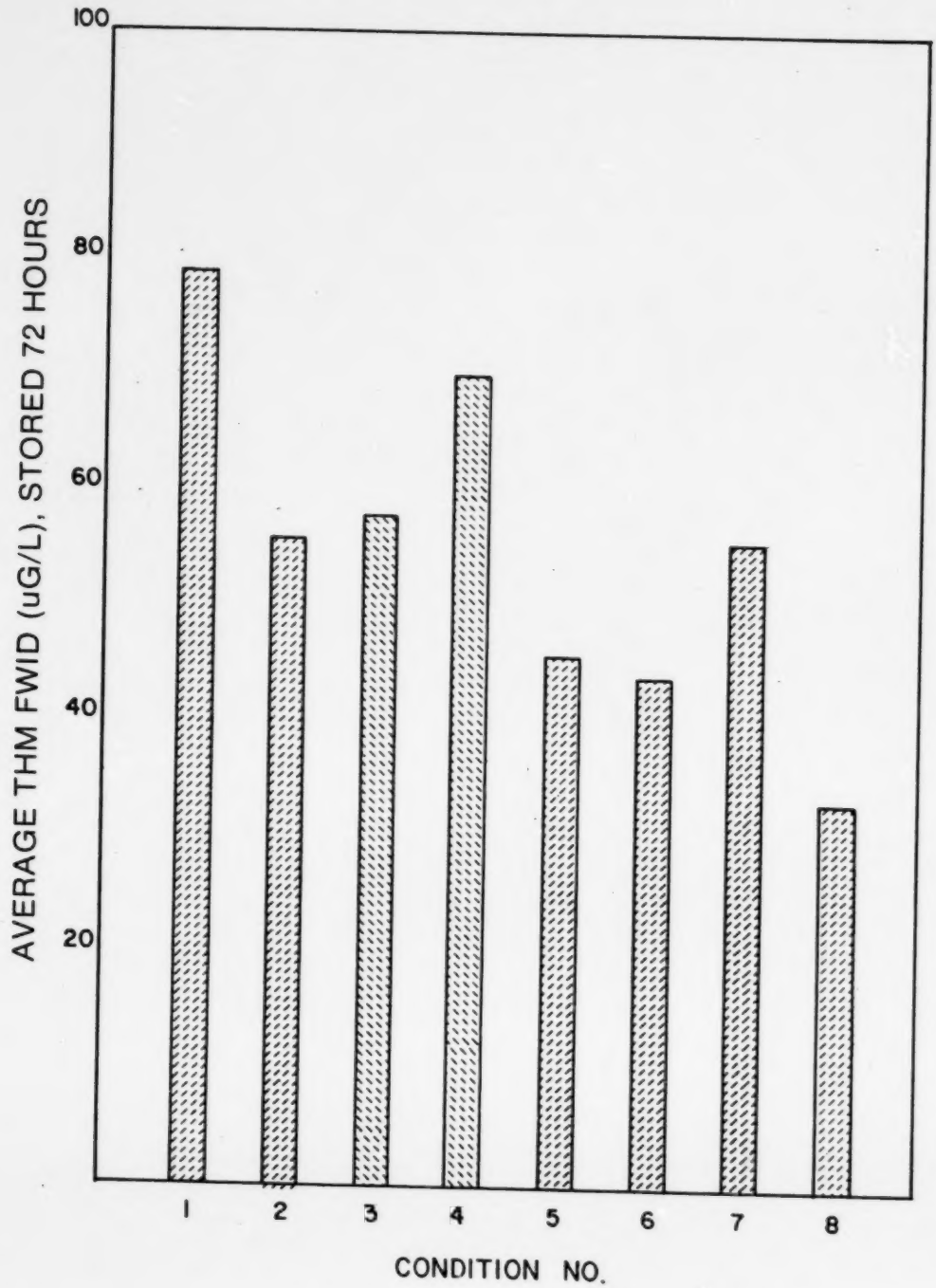
DAYTONA BEACH PILOT PLANT STUDY

FIGURE 23 Raw water super chlorinated.



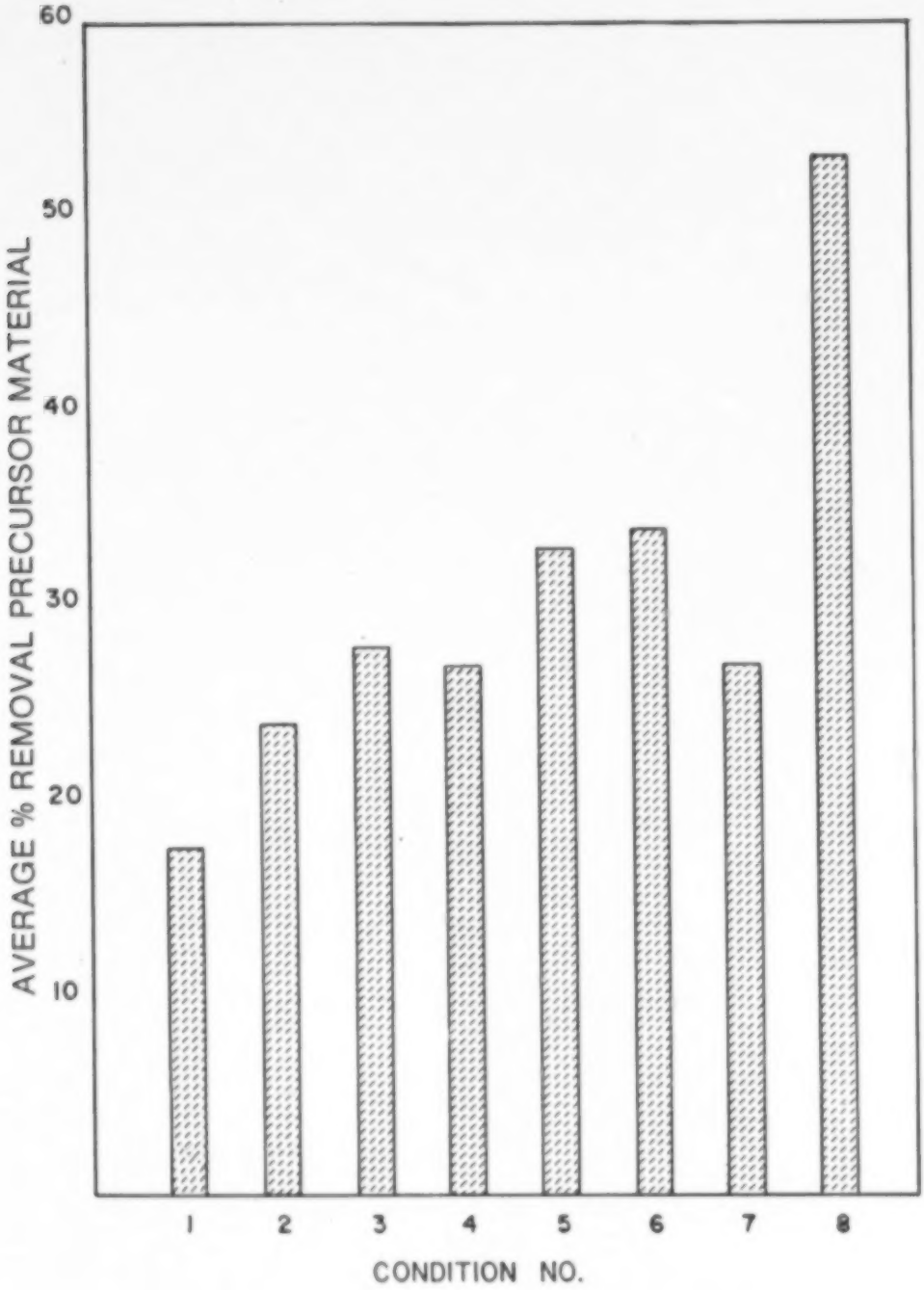
DAYTONA BEACH PILOT PLANT STUDY

FIGURE 24 Finished water super chlorinated.



DAYTONA BEACH PILOT PLANT STUDY

FIGURE 25 THM finished water immediately dechlorinated.



DAYTONA BEACH PILOT PLANT STUDY

FIGURE 26 Average % removal precursor material $\left(\frac{RWSC-FWSC}{RWSC}\right)$.

TABLE 7. THM FORMATION POTENTIAL OF COAGULATING CHEMICALS

Chemical	Concentration	Cl_2 dose	TTHMs ug/L	Time Stored
Clay (Ca35)	2704 mg/l	20 mg/l	228	72 hrs
XE-391	1.1% solids	20 mg/l	2.06	72 hrs.
XE-392	6.5% solids	20 mg/l	22.3	72 hrs.
XE-391	1.1% solids	0 mg/l	1.27	0 hrs.
XE-392	6.5% solids	0 mg/l	1.85	0 hrs.
Alum	50 mg/L	6 mg/l	72.7	72 hrs.
Liquid Alum	50% W/V	0 mg/l	9.58	0 hrs.
Lime (slaked)	9%	0 mg/l	13.9	0 hrs.

Results of samples of coagulants used during this study chlorinated and analyzed for THM.

RELATIONSHIP BETWEEN THM CONCENTRATION AND TOC AND UV ABSORBANCE

Through part of the study, both TOC and UV absorbance were measured on influent and effluent samples in addition to THM concentrations. The analytical data for these analyses are shown in Tables 8 and 9.

The data for THM vs. TOC, and THM vs. UV absorbance were correlated using the standard correlation coefficient defined by using $X'i = Xi - \bar{X}$ and $Y'i = Yi - \bar{Y}$ where Vxy (correlation coefficient) $= \left[\frac{\Sigma X'i\ Y'i}{\sqrt{\Sigma (X'i)^2\ \Sigma (Y'i)^2}} \right]$

The r always lies between -1 and +1, the extreme being reached only if all points lie exactly on a slanting straight line.

The correlation value between THM and TOC concentration was 0.67. The value, although not a good enough correlation to allow the use of TOC as a surrogate parameter for THMs, indicates that samples with higher TOC levels will tend to have higher THM values. This is not a surprising conclusion since it is known that organic compounds act as precursors for THM formation.

The correlation coefficient between THM and UV absorbance was 0.062. This value indicates very little correlation between the two.

The difficulty in using either THM or TOC concentrations to predict their counterparts is readily apparent when these results are shown graphically as in Figure 27. Similarly, Figure 28 is the graphic representation of the data presented in table 8 and shows the poorer THM/UV correllation.

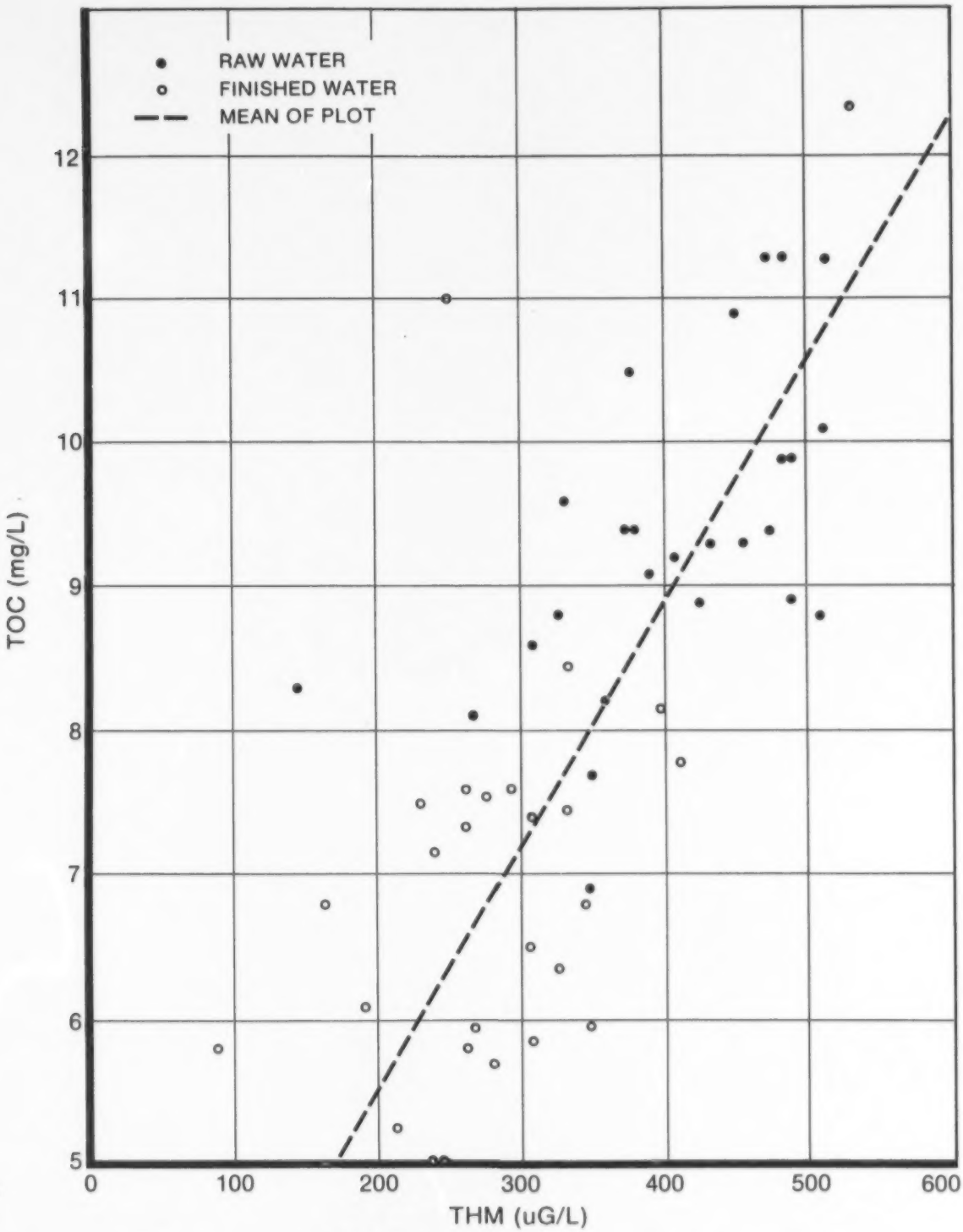


FIGURE 27 THMs vs. TOC for Daytona Beach water samples.

TABLE 8. THMs vs. TOC FOR DAYTONA BEACH WATER SAMPLES

Date	Sample Type	TOC mg/L	UV	THM ug/L
6/25/81	Raw	9.1/8.8		437
6/25/81	Fin	7.1/7.0		342/322
6/29/81	Raw	8.6		307
6/29/81	Fin	6.3/9.3		427/394
7/05/81	Fin	6.4/6.6		305
7/06/81	Raw	9.9		490
7/06/81	Fin	7.8/7.3		294
7/07/81	Raw	8.9		490
7/07/81	Fin	8.0/8.3		397
7/08/81	Raw	11.3		482
7/08/81	Fin	9.2/7.7		333
7/09/81	Raw	9.3		458
7/09/81	Fin	5.6/6.1		306
7/12/81	Raw	8.8		510
7/12/81	Fin	7.2/7.6		302/304
7/20/81	Raw	9.4		477
7/20/81	Fin	7.3/7.6		332
7/21/81	Raw	8.9		425
7/21/81	Fin	6.7/6.9		343
7/22/81	Raw	10.1		512
7/22/81	Fin	6.0/6.7		325
7/23/81	Raw	9.9		482
7/23/81	Fin	7.4/7.3		260
7/27/81	Raw	9.8		
7/27/81	Fin	8.0/8.1		
7/28/81	Raw	11.3		476
7/28/81	Fin	5.8/5.6		280
7/29/81	Raw	9.1		390
7/29/81	Fin	4.8/5.2		239
7/30/81	Raw	10.5		379
7/30/81	Fin	7.5/7.7		260
8/11/81	Raw	11.8	0.311	
8/11/81	Fin	9.0/9.2	0.214/0.076	
8/12/81	Raw	11.3	0.335	516
8/12/81	Fin	10.7/11.3	0.348/0.158	248
8/13/81	Raw	10.9	0.232	450
8/13/81	Fin	12.9/11.8	0.135/0.129	533
8/17/81	Raw	9.3	0.261	435

TABLE 8. Continued

Date	Sample Type	TOC mg/L	UV	THM ug/L
8/17/81	Fin	8.1/7.0	0.125/0.123	274
8/18/81	Raw	9.2	0.254	406
8/18/81	Fin	7.9/7.1	0.116/0.120	233
8/19/81	Raw	9.4	0.248	376
8/19/81	Fin	7.0/6.9	0.132/0.129	347
9/01/81	Raw	8.1	0.256	
9/01/81	Fin	6.4/6.1	0.170/0.165	
9/02/81	Raw	8.2	0.260	359
9/02/81	Fin	4.8/5.7	0.087/0.094	213
9/03/81	Raw	8.1	0.260	
9/08/81	Raw	8.3	0.250	143
9/08/81	Fin	5.6/6.0	0.125/0.115	87*
9/08/81	Raw	8.1	0.251	266
9/08/81	Fin	5.7/5.9	0.118/0.118	260
9/10/81	Raw	7.7	0.239	349
9/10/81	Fin	5.0/5.0	0.095/0.099	241
9/14/81	Raw	6.9	0.245	346
9/14/81	Fin	7.7/7.2	0.094/0.096	239
9/15/81	Raw	9.6	0.253	331
9/15/81	Fin	6.8/6.8	0.102/0.100	162
9/16/81	Raw	9.4	0.276	
9/16/81	Fin	6.4/6.2	0.113/0.092	
9/17/81	Raw	8.8	0.280	324
9/17/81	Fin	6.2/6.0	0.101/0.100	191
9/18/81	Raw	9.4	0.253	380
9/18/81	Fin	5.8/6.1	0.095/0.097	265

NOTE: No record of TOC's collected on 10/19/81 and 10/20/81.

No record of TOC results collected on 9/28, 9/29, 10/15, 10/18 11/08, 11/11, 11/12/ 11/16, 11/17, 11/18 and 11/19/81.

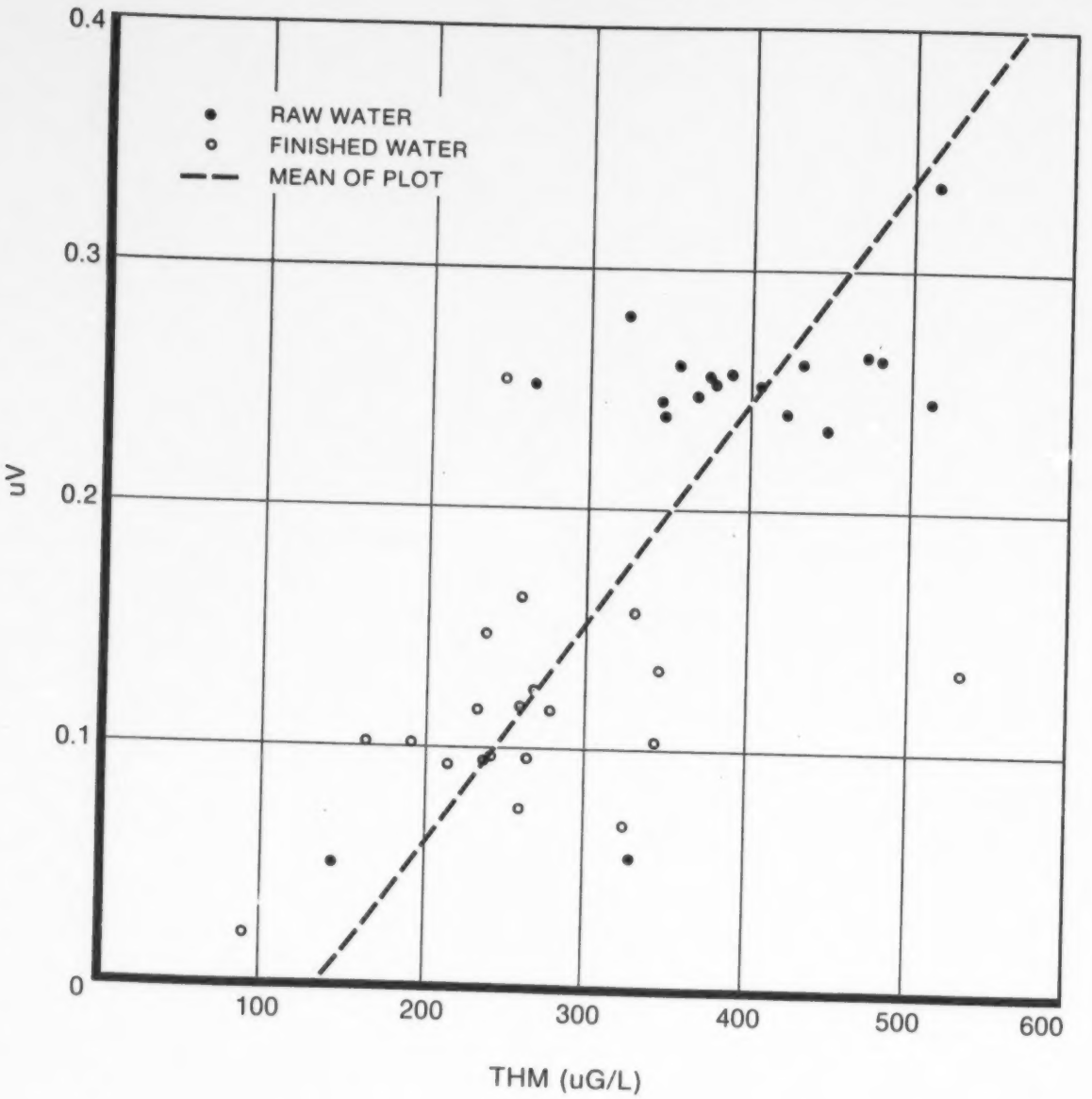


FIGURE 28 THMs vs. uV for Daytona Beach water samples.

TABLE 9. THMs vs UV FOR DAYTONA BEACH WATER SAMPLES

Date	Sample Type	UV	THM ug/L
7/20/81	Raw	9.4	
7/20/81	Fin	7.3/7.6	0.152/0.154
7/21/81	Raw	0.240	425
7/21/81	Fin	0.100/0.105	343
7/22/81	Raw	0.245	512
7/22/81	Fin	0.076/0.066	325
7/23/81	Raw	0.262	482
7/23/81	Fin	0.138/0.006	260
7/28/81	Raw	0.263	476
7/28/81	Fin	0.115/0.115	280
7/29/81	Raw	0.257	390
7/29/81	Fin	0.214/0.082	239
7/30/81	Raw	0.255	379
7/30/81	Fin	0.156/0.166	260
8/12/81	Raw	0.335	516
8/12/81	Fin	0.348/0.158	248
8/13/81	Raw	0.232	450
8/13/81	Fin	0.135/0.129	533
8/17/81	Raw	0.261	435
8/17/81	Fin	0.125/0.123	274
8/18/81	Raw	0.254	406
8/18/81	Fin	0.016/0.120	233
8/18/81	Raw	0.248	376
8/19/81	Fin	0.132/0.129	347
9/02/81	Raw	0.260	359
9/02/81	Fin	0.087/0.094	213
9/08/81	Raw	0.250	143
9/08/81	Fin	0.125/0.115	87
9/09/81	Raw	0.251	266
9/08/81	Fin	0.118/0.118	260
9/10/81	Raw	0.239	349
9/10/81	Fin	0.095/0.099	241
9/14/81	Raw	0.245	346
9/14/81	Fin	0.094/0.096	239
9/15/81	Raw	0.253	331
9/15/81	Fin	0.102/0.100	162

TABLE 9. Continued

Date	Sample Type	UV	THM ug/L
9/17/81	Raw	0.280	324
9/17/81	Fin	0.101/0.100	191
9/18/81	Raw	0.253	380
9/18/81	Fin	0.095/0.097	265

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APPENDIX A

EXPERIMENTAL PROCEDURES

TABLE NO. 10

ANALYSIS METHODS

1. Color:

   Reference 8, p. 60, 204A. Visual Comparison Method.

2. Turbidity:

   Reference 8, p. 132, 214A. Nephelometric Method - NTU's.

   Instrument - Ratio Turbidimeter Hach Model 18900

3. Aluminum:

   Reference 9, p. 2-7, Alumino Method Using Alu Ver III Aluminum Reagent For Water, APHA Standard Methods, 12th ed., 1965.

   Instrument - Bausch & Lomb Spectronic 20 Spectrophotometer

4. Hardness:

   Reference 8, p. 195, 314B. EDTA Titrimetric Method.

5. Chlorine Residual:

   Reference 8, p. 289, 408D. DPD Ferrous Titrimetric Method.

6. pH:

   Reference 8, p. 402, 423 pH Value.

   Instrument - Orion Model 601A Digital Ionalyzer

7. Trihalomethanes:

   Reference 10, Liquid/Liquid Extraction, Method 501.2.

Instrument - Hewlett-Packard Model 5840A Gas Chromatograph with Electron Capture Detector. THMFP refers to sample without buffering or pH adjustment, chlorinated, and stored for 72 hours at ambient temperature.

8. Alkalinity:

   Reference 8, p. 253, 403 Alkalinity.

9. Total Organic Carbon (TOC) Analysis:

   Reference 11, Total Organic Carbon, Method 415.1.

   Instrument - Oceanographic International Corp., Model 524-B

10. Ultraviolet (UV) Absorbance:

    UV absorbance was determined by the following method:

    a. The pH was adjusted to 4.0 with 0.1 N HCl and 0.019 N H_2SO_4.

    b. Samples were centrifuged.

    c. The UV absorbance was read at 254 nm using the Perkin Elmer Model 552 Spectrophotometer.

    No "standard" method currently exists for UV absorbance. The method used here is similar to the method used in several other THM precursor studies and therefore will allow for a direct comparison of data with those developed in other studies.

APPENDIX B

JAR TEST PROCEDURE

GENERAL COMMENTS

Mix Time - Review of design specifications for the Eimco Softeners used in this plant indicates that at the maximum design capacity of 22.7 MLD, (6 MGD) flow rate is approximately a 1.26 minute detention time in the rapid mix area of the softener and a slow mix time of approximately 13.6 minutes. Therefore, it is recommended that a rapid mix time of 1 minute and a slow mix time of 5 minutes be used in jar testing, with a final 5 minutes allowed for settling.

Lime Addition - pH control is often a problem in jar testing. Reagent grade $Ca(OH)_2$, which works well under jar test conditions, does not reflect plant conditions as well as might be desirable (plant operators frequently report that different bulk loads of lime react differently in the softeners--although CaO percentages are the same). For the purposes of jar testing, it is recommended that a CaO sample from the storage silos be analyzed for percentage CaO and a predetermined amount (based on % CaO) of this lime be weighed to add directly to each jar. Jar tests run in the lab show this method to work very well, although NaOH (1N) often must be added dropwise for final pH adjustment.

Polymer Addition - Because of the extremely high viscosity of many polyelectrolytes available for use as coagulants/flocculants, addition of precise amounts of these chemicals is very difficult in the jar tests. Polymer adheres to pipette walls and makes accurate delivery impossible. We have found that by using disposable plastic syringes the amount of material adhering to the walls of the syringe barrel can be quickly removed by flushing the syringe with dilution water. This practice also facilitates polymer dilutions since the act of drawing the delivered polymer back into the syringe barrel along with dilution water and delivering the mixture several times gives an excellent mix much more rapidly than the more conventional methods of using mechanical stirrers.

GENERAL PROCEDURE

The following step-wise procedure was used during the duration of this study:

1. Prepare dilutions of coagulants to be evaluated. Determine dilutions so that no less than 1 ml nor more than 30 mls are

added to any one jar. Add enough dilution water to these solutions so that the same solution volume is added to each jar.

2. Fill jars to the 1.5 or 2.0 liter mark with water to be treated.

3. Weigh (using an analytical balance) 220 mg of CaO to be added to each 1 liter solution in each jar. Add this amount to each jar and allow time for dissolution of the lime. Adjust final pH with 1N NaOH to pH 9.4 if necessary.

4. Set jar tester to highest speed for "flash mix" and add chemicals as quickly as possible. Allow 10 seconds flash mix.

5. For Phipps and Bird jar tester use a speed of 100 rpm for rapid mix for one minute.

6. Reduce speed to 50 rpm for five minutes of slow mix.

7. Allow jars to settle for five minutes with no mixing.

8. Siphon samples from at least 2 inches below liquid surface.

This is a very general procedure and may be altered considerably depending on the conditions to be evaluated.

APPENDIX C

SAMPLING PROCEDURES

Sampling under each set of pilot plant conditions was conducted when the pilot plant had stabilized to where the desired operating parameters fell within a predetermined range. Samples were not collected when, due to plant upset or mechanical problems, operating parameters fell outside of this range.

Samples collected each day were analyzed for the following:

1. pH, free Cl_2 residual, total hardness, alkalinity, turbidity, color - these analyses were performed to collect data on plant operation and were used to control plant operation.

2. TOC - Samples were collected of the raw water and finished water in duplicate and shipped (refrigerated) to a commercial laboratory along with a sample blank. Samples were analyzed within 24 hours using an Oceanography Model 524-B TOC Analyzer.

3. UV Absorbance - Unused duplicate samples shipped for TOC analysis were analyzed for U.V. absorbance by the same laboratory using a Perkin Elmer Model 222 spectrophotometer.

4. THM - Samples of the raw water, settled water, sludge (once per condition), and pilot plant effluent samples were analyzed for THMs using a Hewlett Packard Model 5840 gas chromatograph equipped with an electron capture detector.

TOC, UV absorbance, and THM samples were collected headspace free in 2 oz. amber glass bottles (Pierce #19832) and sealed with PTFE faced silicon septa by means of plastic screw caps. All THM samples, with the exception of the raw unchlorinated samples, were chlorinated using the chlorine gas in water solution fed at the Ralph F. Brennan Plant. Solution strength typically fell in the 1200 to 1300 mg/L range and was analyzed daily prior to use. Sufficient chlorine was added to the samples to ensure a free chlorine residual (0.2 mg/l Florida minimum requirement) after 72 hours. Sample pH was not adjusted. Dechlorination of samples was accomplished by the addition of 4.5 mg of sodium thiosulfate to each 60 ml sample. This amount was

verified as being sufficient for the sample volumes and Cl_2 residuals used during this project. Samples to be stored three days prior to quenching with sodium thiosulfate were stored in the dark at ambient temperture in a tray of activated carbon. After quenching, samples were refrigerated until analyzed. Analysis was performed within 14 days.

APPENDIX D

PILOT PLANT DESCRIPTION

The U.S. Environmental Protection Agency Mobile Pilot Water Treatment Plant consists of two identical water treatment systems installed in a 12.8m long trailer. The plant is fabricated of stainless steel. The design critieria for each unit are:

Discharge:	Q = .32 Lps
Rapid Mix:	1 - 2 minutes
Flocculation:	30 - 60 minutes
Settling:	3 - 6 hours
Filtration Flow Rate:	0.5 Lps/ft^2

The plant has been designed for the following treatment processes: chemical coagulation and flocculation, sedimentation, filtration, and disinfection.

Because the plant consists of two hydraulically separate treatment plants, two simultaneous tests can be run, (or the units can be run in series), to test the effect of 2-stage treatment methods. The general layout of the water treatment plant inside the trailer is shown in Figure 1.

Raw water is pumped from the raw water source into the constant head tank. Two stainless steel centrifugal pumps transfer water from the constant head tank to the rapid mix tanks of each treatment system through valves and flow meters for flow adjustment.

The rapid mix tank of each system is a 37.8L cylindrical tank .38m feet in diameter and .46m high. The water discharges from the rapid mix through a 2.54cm diameter pipe. The mixer drive for each rapid mix is a D.C. variable speed Bodine fractional gear motor.

The flocculation tank was designed to provide gentle stirring to a flow of .32 liters per second with a 40-minute detention time. The .9m square and 1.1m high flocculation tank provides a water depth of .9m. The total waste volume is .76cm. The tank is divided into four chambers, each with its own variable speed mechanical mixer, allowing for tapered flocculation. The water exits the flocculation tank through a 2.54cm diameter pipe.

The clarifier is 3m long, 1.2m wide, and 1.7m high. With a water depth of 1.4m and a flow rate of .32 Lps the detention time is 4.4 hours. The flow entering the clarifier is diverted downward by a baffle to discourage short-circuiting.

The effluent trough can be moved longitudinally along the water surface for maximum efficiency. The effluent trough is equipped with V-notches 2.54cm deep.

The settled water flows from the collection trough through a 2.54cm diameter flexible Tygon tubing to a collection box on the side of the clarifier. The storage capacity of the collection box reduces fluctuations of the discharge through the filtration columns and gives entrapped air bubbles a chance to escape through the top.

The settled water is pumped from the collection box to the filter columns. The filters are constructed of stainless steel. Each filter unit is .3m by .2m in cross-section and 1.8m deep . The design flow rate for each unit is .16 Lps. The filtration loading rate is 2.6 Lps/sm. Design flow is obtained using two filter units in parallel. Glass ports are provided to observe the filter media.

The filtered water flows to the clearwell. The clearwell measures 1.8m long by 1.5m high by .3m wide. The capacity of the tank is 530 L (140 gallons). The clearwell is also made of stainless steel. A 15cm by 15cm opening in the top is provided for adding chemicals and for inspection. A mixer with three paddles is mounted in the center of the tank. It provides rapid mixing of disinfectants introduced into the tank.

The pilot plant was designed and constructed by faculty, staff, and students at the University of Missouri-Columbia, under a research project funded by the U.S. Environmental Protection Agency. It has continued to provide a valuable research tool on various research projects such as the subject project. Additional information on this pilot plant can be obtained from the Municipal Environmental Research Center, U. S. Environmental Protection Agency, Cincinnati, Ohio.